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A TEXTBOOK OF PHYSICS

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A TEXTBOOK OF PHYSICS

BY

E. GRIMSEHL

EDITED BY

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VOL. V

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FROM THE PREFACE TO THE SEVENTH GERMAN EDITION

The subject of this volume is the relationship between matter and ether, as expressed in the electrical structure of matter, and in the interaction of matter and radiation.

Various considerations, combined with experience gained in lecturing, have led me to choose the historical method of dealing with the interaction of atoms and radiation fields—a branch of the subject which, thanks to wave mechanics, may be regarded as having nearly reached the end of one stage of its development. Even yet the Rutherford-Bohr model of the atom gives in many cases a convenient first approximation, and a ready means of assimilating the essential facts. At the same time, wave mechanics has reached a sufficient degree of development to be capable of indicating not only the limitations of the Bohr model, but also the method of making the necessary corrections.

As in the earlier volumes of this textbook, I have striven consistently to keep experimental facts in the foreground, and to carry theory only so far as it is needed in order to explain experimental results.

The present volume is in this edition to all intents and purposes a completely new work, only a few sections on temperature radiation and radioactivity having been taken over from the earlier editions.

R. TOMASCHEK.

DRESDEN,
August, 1934.

PREFACE TO THE ENGLISH EDITION

I have taken the opportunity of the publication of this edition to make a few corrections and improvements. With a view to meeting the needs of English readers, some new matter has been added. I wish to thank the translator for the adequate manner in which he has carried out his task, and hope that in its new dress the work will greatly extend the circle of its friends.

R. TOMASCHEK.

DRESDEN,
August, 1935.

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PHYSICS OF THE ATOM

CHAPTER I

The Electrical Structure of Matter

A. THE ELEMENTARY CONSTITUENTS OF MATTER

1. Experimental Evidence for an Electrical Structure of Matter

Probably the first indication that electricity and matter are closely related was Faraday's discovery (1837) that the forces arising from electric charges are altered if the space surrounding them is filled with matter. The quantitative measure of this effect is the *dielectric constant*, and it has already been explained at length in Vol. III (p. 99 *et seq.*) how this effect of matter upon electric fields may be visualized. It was shown that the change observed in the field is caused either by the displacement of electric charges in the atoms or molecules of the material substance, or else by the more or less complete orientation of *dipoles* (or more complicated charge distributions) which were present from the first and which had been brought into random directions as a result of thermal motions. Attention was also drawn to the fact that the magnitude of the charges involved is of the order of the elementary charge.

In the phenomena of pyro- and piezo-electricity (Vol. III, pp. 94 and 95) we have likewise become acquainted with facts which show that in crystals, which by their very shapes bear evidence of a certain regularity of structure, such dipoles (or more complicated charge distributions) must in many cases be arranged in an orderly manner, even in the absence of an external field.

Faraday's second fundamental law of electrolysis (Vol. III, p.155) shows further that the quantity of electricity transported through electrolytes bears a definite quantitative relationship to the number of transporting particles. To-day we can formulate this relationship as follows:

In electrolysis each ion carries a number of elementary electric charges (positive or negative) corresponding to its chemical valency.

Further evidence for the intimate connexion between chemical properties and electric charge is to be found in the chemical differences between the differently charged ions (e.g. Cu^{++} and Cu^{+}) derived from the same element, and still more strikingly in the remarkable chemical differences between an uncharged atom and the corresponding ion as observed in solutions. The fact that ionic charges are always integral multiples of the elementary charge makes it very probable that these elementary charges play an essential part in the structure of ions and atoms.

The correctness of these conclusions is firmly established by the results of MILLIKAN's experiment (Vol. III, p. 48). The changes in the charge of the droplet during observation are always found to be abrupt jumps of one elementary charge or an integral number of such charges. This leads to the view that the value of the charge of a univalent ion found in electrolysis is not a statistical mean, but is actually the magnitude of an invariable elementary quantum of electricity.

The isolation of negative elementary charges, or **electrons,** free from material carriers (e.g. as cathode rays, Vol. III, p. 330) proves that these charges are capable of an independent existence apart from matter; they then have the properties of discrete corpuscles * to which we ascribe a certain inertia or mass (Vol. III, p. 322).

These electrons obviously form *constituents of matter*; for it is possible (as has already been mentioned in Vol. III and as will be discussed in detail below) to liberate them from matter in various ways (Vol. III, p. 312), e.g. by heating, by illumination, or by bombardment with material particles or rapidly moving electrons. In all these cases detailed investigation (by the electric and magnetic deflections, Vol. III, p. 314) shows that the particles concerned are all of one kind, namely, elementary negative quanta of electricity possessing equal charges and masses.

The existence of electrons in the interior of matter is further proved directly by the experiments of TOLMAN (Vol. III, p. 361), who determined the specific charge of the carriers in metals. The most important evidence, however, is derived from the phenomena of the emission and absorption of light (or, more generally, of electromagnetic waves) and of the passage of light through matter. These subjects are discussed in the present volume.

One of the most important and illuminating contributions in this connexion was the discovery, through the investigation of the effect of a magnetic field on the emission of light (the ZEEMAN effect (1896); see Vol. IV, p. 256, and this volume, p. 203), that the charges responsible for the emission of light by matter are negative elementary charges or electrons.

* Lat. *corpuscula,* a particle.

2. The Problem of Atomic Structure

The Elementary Constituents of Matter.—The evidence outlined in the preceding section proves beyond doubt that the electron, with its charge of $1{\cdot}59 \times 10^{-19}$ coulomb and mass of $m_0 = 8{\cdot}98 \times 10^{-28}$ gm., is a constituent of matter. Comparison of the mass of an electron with that of a hydrogen atom, namely, $m_H = 1{\cdot}662 \times 10^{-24}$ gm., shows that the former is very much the smaller. Now it has never been found possible (e.g. in positive-ray experiments or in electrolysis) to obtain hydrogen ions in which the original neutral hydrogen atom has lost more than one electron. From this we conclude that the hydrogen atom contains only *one* electron. The hydrogen ion H^+, however, is the lightest material particle ever found. Matter subdivided into smaller masses than $H^+ = 1{\cdot}661 \times 10^{-24}$ gm. is unknown. The hydrogen ion carries a *positive* charge equal in magnitude to the negative charge of an electron, and is called a **proton.** Whether the mass of the proton is of purely electromagnetic nature like that of the electron, and indeed whether such a question has any real meaning, as yet remains unknown (see below).

Without further evidence it is in the nature of a hypothesis to assume, as Prout did (1815–16), that hydrogen atoms (or, in the light of our modern knowledge, protons) are elementary constituents of matter. If this hypothesis is true, we deduce at once that the atomic weights of the chemical elements must be integral multiples of the atomic weight of hydrogen. Since the chemical evidence shows that this is not the case, the hypothesis was at first quite rightly abandoned.

Unexpectedly, however, the experiments of Aston (Vol. III, p. 345, and this volume, p. 102) showed that the masses of individual atoms are actually multiples of the mass of the hydrogen atom and that the majority of the chemical elements consist of a mixture of chemically similar atoms of different masses (*isotopes*). For the very small deviations see p. 104.

Thus material bodies are made up of *protons* and *electrons*. Recently other particles have been observed (p. 111) which, though *neutral* and possessing approximately the mass m_H, are not hydrogen atoms. They are called **neutrons.** They are perhaps to be regarded as very close unions of protons and electrons; it is possible, however, that their nature is quite different, in which case they would have to be regarded as a third constituent of matter (p. 106).

Since protons and electrons attract one another with extremely large forces *, there must be repulsive forces at work within the atoms in order to preserve equilibrium. The nature of these forces

---

* The Coulomb force of attraction between two elementary charges, assumed to be points, at a distance of 10^{-8} cm. apart (the approximate magnitude of atoms, cf. Vol. II, p. 53) is $2{\cdot}27 \times 10^{-3}$ dyne. The sum of the forces for one gramme-atom of hydrogen atoms is therefore 14×10^{20} dynes or 1400 billion kg. wt.

TABLE I.—THE PERIODIC TABLE OF THE ELEMENTS

The numbers preceding the symbols are the atomic numbers. Below them are the atomic weights.

Period	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII	Group O
I	**1** H 1·008								**2** He 4·00
II	**3** Li 6·94	**4** Be 9·02	**5** B 10·82	**6** C 12·00	**7** N 14·008	**8** O 16·00	**9** F 19·00		**10** Ne 20·18
III	**11** Na 23·00	**12** Mg 24·32	**13** Al 26·97	**14** Si 28·06	**15** P 31·02	**16** S 32·06	**17** Cl 35·46		**18** A 39·94
IV	**19** K 39·096	**20** Ca 40·08	**21** Sc 45·10	**22** Ti 47·90	**23** V 50·95	**24** Cr 52·01	**25** Mn 54·93	**26** Fe 55·84 **27** Co 58·94 **28** Ni 58·69	
	29 Cu 63·57	**30** Zn 65·38	**31** Ga 69·72	**32** Ge 72·60	**33** As 74·91	**34** Se 78·97	**35** Br 79·92		**36** Kr 83·7
V	**37** Rb 85·44	**38** Sr 87·63	**39** Y 88·92	**40** Zr 91·22	**41** Cb 93·3	**42** Mo 96·0	**43** Ma (98)	**44** Ru 101·7 **45** Rh 102·9 **46** Pd 106·7	
	47 Ag 107·88	**48** Cd 112·4	**49** In 114·8	**50** Sn 118·7	**51** Sb 121·8	**52** Te 127·6	**53** I 126·93		**54** Xe 131·3
VI	**55** Cs 132·9	**56** Ba 137·4	**57–71** Rare earths	**72** Hf 178·6	**73** Ta 181·4	**74** W 184	**75** Re 186·3	**76** Os 191·5 **77** Ir 193·1 **78** Pt 195·2	
	79 Au 197·2	**80** Hg 200·6	**81** Tl 204·4	**82** Pb 207·2	**83** Bi 209·0	**84** Po (210)	**85** —		**86** Rn 222
VII	**87** —	**88** Ra 226·0	**89** Ac (227)	**90** Th 232·1	**91** Pa (231)	**92** U 238·1			

Rare earths	**57 La** **138·9**	**58 Ce** **140·1**	**59 Pr** **140·9**	**60 Nd** **144·3**	**61 Il** **—**	**62 Sm** **150·4**	**63 Eu** **152·0**	**64 Gd** **157·3**	**65 Tb** **159·2**	**66 Dy** **162·5**	**67 Ho** **163·5**	**68 Er** **167·6**	**69 Tm** **169·4**	**70 Yb** **173·0**	**71 Lu** **175·0**

still remains unknown. By analogy with the stability of the solar system we may assume the existence of centrifugal forces, and suppose that the charges revolve round one another. Certain facts connected with magnetism lend support to this theory. Alternatively we may suppose the cause of the repulsion to lie in vortex motions situated in the elementary charges themselves (Vol. III, p. 50). Perhaps both these causes are operative. There is no doubt, however, that some kind of *motion* is going on inside atoms; the equilibrium is dynamic, as is shown by the "spin" properties of the elementary constituents (p. 312).

Periodic Properties of the Elements.—The fact that the difference between the elements, e.g. between iron and gold, is due only to a difference in the number and arrangement of identical elementary particles, is brought out with especial clearness if we consider the similarities and relationships which exist among the elements. Thus, for example, all the alkaline earth metals, Be, Mg, Ca, Sr, Ba, Ra, exhibit great chemical similarities, in spite of their very different atomic weights. They are all chemically divalent, strongly electropositive, metallic, have rather low melting-points and boiling-points, low densities, similar spectra, and so on.

If the elements are numbered in the order of increasing atomic weight, it is found that the differences between the numbers belonging to successive alkaline earth metals are respectively 8, 8, 18, 18, and 32. Most of the other groups of related elements give the same series of differences. All these relationships find expression in the so-called *periodic table*, which is reproduced in Table I. In this the elements are arranged from left to right in the order of increasing atomic weight. Elements which are related to one another fall into vertical " groups ". It is found that in this way all the elements can be satisfactorily accommodated in definite places, although in order to accomplish this it is necessary in three cases (A—K; Co—Ni; Te—I) to invert the order of atomic weights. These inversions are definitely dictated by the chemical and other properties of the elements in question, and indicate that the atomic weight is not really the characteristic quantity underlying the properties which are summarized in the periodic table. This matter will be explained later (p. 76). It is also found that two places in the table must be left vacant. These obviously belong to elements which have not yet been discovered. When the table was originally compiled (LOTHAR MEYER and MENDELÉEFF) there were a number of vacant places. All except the two just mentioned have been filled by newly-discovered elements possessing the properties anticipated. Each element can accordingly be given a number, the **atomic number** Z, according to its position in the periodic table. In Table I the atomic number of each element immediately precedes the symbol, while the atomic weight is given below. For the names of the elements see Table II.

TABLE II.—THE ELEMENTS AND THEIR ATOMIC WEIGHTS

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Aluminium	Al	13	26·97	Molybdenum	Mo	42	96·0
Antimony	Sb	51	121·76	Neodymium	Nd	60	144·27
Argon	A	18	39·944	Neon	Ne	10	20·183
Arsenic	As	33	74·91	Nickel	Ni	28	58·69
Barium	Ba	56	137·36	Nitrogen	N	7	14·008
Beryllium	Be	4	9·02	Osmium	Os	76	191·5
Bismuth	Bi	83	209·00	Oxygen	O	8	16·0000
Boron	B	5	10·82	Palladium	Pd	46	106·7
Bromine	Br	35	79·916	Phosphorus	P	15	31·02
Cadmium	Cd	48	112·41	Platinum	Pt	78	195·23
Caesium	Cs	55	132·9	Potassium	K	19	39·10
Calcium	Ca	20	40·08	Praseodymium	Pr	59	140·92
Carbon	C	6	12·00	Radium	Ra	88	225·97
Cerium	Ce	58	140·13	Radon	Rn	86	222
Chlorine	Cl	17	35·457	Rhenium	Re	75	186·31
Chromium	Cr	24	52·01	Rhodium	Rh	45	102·91
Cobalt	Co	27	58·94	Rubidium	Rb	37	85·44
Columbium	Cb	41	93·3	Ruthenium	Ru	44	101·7
Copper	Cu	29	63·57	Samarium	Sm	62	150·43
Dysprosium	Dy	66	162·46	Scandium	Sc	21	45·10
Erbium	Er	68	167·64	Selenium	Se	34	78·97
Europium	Eu	63	152·0	Silicon	Si	14	28·06
Fluorine	F	9	19·00	Silver	Ag	47	107·880
Gadolinium	Gd	64	157·3	Sodium	Na	11	22·997
Gallium	Ga	31	69·72	Strontium	Sr	38	87·63
Germanium	Ge	32	72·60	Sulphur	S	16	32·06
Gold	Au	79	197·2	Tantalum	Ta	73	181·4
Hafnium	Hf	72	178·6	Tellurium	Te	52	127·6
Helium	He	2	4·002	Terbium	Tb	65	159·2
Holmium	Ho	67	163·5	Thallium	Tl	81	204·39
Hydrogen	H	1	1·0078	Thorium	Th	90	232·12
Indium	In	49	114·8	Thulium	Tm	69	169·4
Iodine	I	53	126·92	Tin	Sn	50	118·70
Iridium	Ir	77	193·1	Titanium	Ti	22	47·90
Iron	Fe	26	55·84	Tungsten	W	74	184·0
Krypton	Kr	36	83·7	Uranium	U	92	238·14
Lanthanum	La	57	138·92	Vanadium	V	23	50·95
Lead	Pb	82	207·22	Xenon	Xe	54	131·3
Lithium	Li	3	6·940	Ytterbium	Yb	70	173·0
Lutecium	Lu	71	175·0	Yttrium	Y	39	88·92
Magnesium	Mg	12	24·32	Zinc	Zn	30	65·38
Manganese	Mn	25	54·93	Zirconium	Zr	40	91·22
Mercury	Hg	80	200·61				

The chemical valency is constant throughout each group. As we pass from a given group to the next on the right, the valency with respect to oxygen always increases by one (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7). There is also in the same direction a corresponding increase of the charge on the positive ions of these elements. The valency with respect to hydrogen, on the other hand, decreases by one as we pass from one group to the next on the right (HF, H_2O, NH_3, CH_4), and there is a corresponding decrease in the charge on the negative ions of these elements. The valency characteristic of the group is usually the most important valency exhibited by the elements concerned; but sometimes it is one which, though occurring in certain compounds, is not the commonest or most important (e.g. Cl_2O_7). This is true in particular for the so-called "sub-groups" (e.g. Cu, Ag, Au), which in Table I are slightly displaced relative to the main groups. Thus, for example, Cu is univalent in some compounds, though the commoner valency is two. The reasons for this will be discussed in detail later (p. 341). It is also remarkable that the place for lanthanum (Z = 57) accommodates in addition a group of fifteen elements, the so-called rare earths, which chemically are all extraordinarily similar. The principal valency of the rare earths is three, so that they belong to Group III of the table.

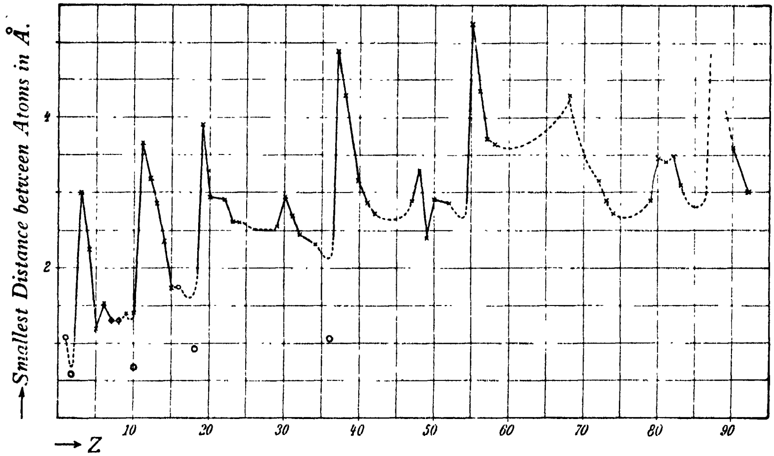

Fig. 1.—Periodicity of effective atomic diameters (the smallest distances between atoms in crystals. The points for hydrogen and the inert gases—shown as circles—refer to the "true" atomic diameters calculated from ionization potentials).

Group O contains the inert gases, which do not react chemically at all. In the form of the periodic table given in Table I the corresponding sub-group is formed by the so-called Group VIII; this contains elements which may exhibit a valency of eight, but may also in certain circumstances be very inert chemically (the platinum metals; "passive" iron, cobalt, and nickel). The inclusion of iron, which is usually di- or trivalent, in this group shows that the form of the periodic table given here is somewhat artificial. For this reason other forms are often preferred, in which the sub-groups do not appear as such but are inserted between the main groups. The so-called "long periods" then extend over 18 groups. A full explanation must be reserved for a subsequent occasion (p. 334). The student cannot be too strongly recommended to keep in his mind's eye the *mutual relationships of the elements* expressed in the periodic table. An intimate acquaintance with this classification forms an effective key to a more complete knowledge of the structure of atoms.

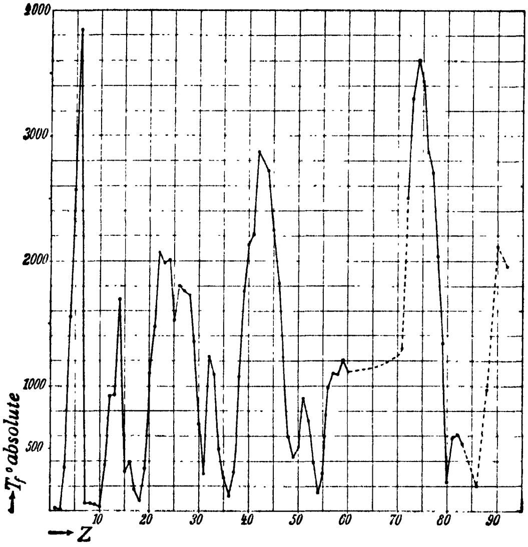

Fig. 2.—Periodicity of melting-points

Two examples may be given to show how marked the periodicity of properties amongst the elements is. In figs. 1 and 2 the abscissæ are atomic numbers, while the ordinates are respectively atomic diameters and melting-points. The remarkable periodicity is at once obvious, and is seen to coincide (maxima in fig. 1, minima in fig. 2) with the principal groups in Table I.

Arrangement of the Elementary Constituents.—In the light of what has been said above, the manifold differences in matter, as exhibited in the 92 different chemical elements, are to be regarded as due simply to different arrangements of elementary electric charges and masses. The enormous qualitative differences, e.g. between chlorine and iron, must be thought of as resulting from a difference in the number and arrangement of certain fundamental constituents.

Hence our most important problem is that of obtaining a quantitative knowledge of *the number and arrangement of the elementary constituents and of the forces and motions within atoms and molecules.* To some extent it is possible to draw conclusions concerning these quantities from the macroscopic behaviour of matter, i.e. from phenomena involving a very large number of molecules simultaneously (e.g. dielectric constant, &c.). More detailed knowledge is only to be expected, however, from experiments on the behaviour of the electromagnetic fields within the atom. For such experiments it is necessary to use testing bodies which are themselves small as compared with the dimensions of the fields under investigation. Rapidly moving electrons (cathode rays) and corpuscles such as H^+ (protons) and more especially He^{++} (the so-called α-particles) have proved most suitable in this connexion (see pp. 15 and 81). In particular, investigations with cathode rays laid the foundation of the theories outlined above. There is one group of phenomena, however, in which the electrical structure of matter and the enormous energies involved are exhibited spontaneously without human agency. These phenomena, which are classed together under the name of radioactivity, will now be considered in more detail.

B. Radioactivity *

3. Fundamental Phenomena

Historical.—When X-rays were discovered (see Vol. III, p. 347) it was observed that they always emanated from the fluorescent spot on the glass wall of the discharge tube. Acting on the assumption that there must be some intimate relationship between X-rays and fluorescence, H. Becquerel † (1895) made experiments to find out whether the strongly fluorescent *uranium* compounds emit X-rays after bombardment with cathode rays. His anticipations were apparently confirmed, for he found that a piece of potassium uranyl sulphate, which had been exposed to cathode rays and subsequently wrapped up in black paper, blackened a photographic plate upon which it was placed.

To his astonishment he subsequently found (1896) that the uranium compound exhibits this property even in the absence of previous treatment with cathode rays or any other agency. Further investigation showed that the property discovered by Becquerel and now known as **radioactivity** bears no causal relation to fluorescence whatever, but is characteristic of the element uranium itself. Neither exposure to any other kind of rays, nor heating, nor any sort of electrical treatment is required to make uranium radioactive. The uranium gives out its rays " spontaneously ", i.e. without energy being supplied from outside.

The rays emitted by uranium are very similar to X-rays, in that they can pass through opaque objects and blacken a photographic plate thereafter. A further similarity is to be found in the fact that the rays render air conducting. This latter property provides a convenient method for measuring the intensity of the radioactivity and comparing it with the effects of X-rays. Another fact with an important bearing on the investigation of the rays is that they produce a fluorescent glow in certain substances, particularly zinc sulphide containing copper (used in the so-called SIDOT screens).

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* Only the main aspects of radioactivity are treated here. A considerable amount of further information on the subject will be given later; see especially pp. 78, 356.

† Henri Becquerel (1852–1908) was latterly Professor at the École Polytechnique in Paris; his father, Alexandre Edmond Becquerel (died 1891), and his grandfather, Antoine César Becquerel (died 1878), were also well-known physicists.

Radioactivity can be demonstrated in a very simple manner by means of the apparatus shown in Vol. III, fig. 7, p. 302, using a sensitive electrometer. If the potential is taken so high that the saturation current (Vol III, p. 303) is reached, all the carriers generated by the radioactive rays are captured, and the current strength is then a measure of the radioactivity of the substance under investigation. A further very informative method that may be mentioned here is the WILSON cloud-chamber method (Vol. III, p. 311), in which the radioactive rays are made to leave visible tracks. Numerous applications of these methods will be met with in the present volume.

By investigation of the conductivity produced in air, PIERRE CURIE and his wife * found that the radioactivity of **pitchblende** and a few other minerals exceeds that of uranium in intensity. Pitchblende is the mineral from which uranium is chiefly obtained. The residues obtained in the preparation of uranium, previously thrown away as useless, were found to be particularly radioactive, their intensity being about four times that of uranium itself.

The two CURIES quite rightly deduced that these residues must contain some substance with extremely high radioactivity. As their raw material they took the pitchblende residues from Joachimsthal in Bohemia, from which the uranium had been extracted. This they divided into two fractions by chemical methods and investigated which possessed the greater radioactivity. This procedure was then repeated a great many times, the more radioactive fraction being retained each time. In this way they were able as early as 1898 to obtain a substance possessing an activity many thousands of times greater than that of uranium. This substance appeared to be *chemically* identical with bismuth, from which it differed only in its great radioactivity. To the substance giving rise to this activity, which she regarded as a hitherto unknown metal resembling bismuth, Mme CURIE gave the name **polonium**. It has since been found possible to obtain polonium in a chemically pure state.

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* PIERRE CURIE (1859–1906), born in Paris, studied at the Sorbonne, from 1895 to 1900 was Professor of Physics and Chemistry at the Municipal College at Paris, and from 1900 to 1906 Professor at the Sorbonne. Together with his brother JEAN CURIE he discovered and investigated piezo-electricity, i.e. the electrification of crystals as a result of tension or pressure. In 1895 he married MARIE SKLODOWSKA (1867–1934), a former Polish student at the Sorbonne. In 1904 she obtained her doctorate with an extensive memoir on radioactive substances. After the death of her husband in an accident she was appointed to his professorial chair and was made director of the Radium Institute in Paris, and held these posts until her death. Along with her husband and HENRI BECQUEREL she shared the Nobel Prize in Physics in 1904. In 1911 she was awarded the Nobel Prize in Chemistry—the only instance hitherto of a second award.

Only six months later the two CURIES in collaboration with BÉMONT succeeded in separating from the uranium mineral a second very highly radioactive substance, chemically related to barium. This is obtained from pitchblende along with barium by precipitation, after which it is separated from the barium by a very careful process of fractional precipitation. The CURIES succeeded in isolating this new substance in the form of compounds with chlorine and bromine. They named it **radium.** The radioactivity of radium is approximately a million times stronger than that of uranium.

Radium exhibits all the properties of an alkaline earth metal (e.g. it has a very sparingly soluble sulphate and carbonate), and forms the last member of Group II of the periodic table. Its atomic weight (first determined by HÖNIGSCHMID * in 1914) is 225·97; its atomic number is 88.

Radioactive properties nearly as strong as those of uranium are also possessed by **thorium** and its compounds, as was shown almost simultaneously by Mme CURIE and G. C. SCHMIDT † in 1898. This can easily be demonstrated by placing a gas mantle, 99 per cent of which consists of thorium oxide, near a charged electroscope; the electroscope is discharged in a short time.

Of the remaining elements, so far as we know at present, only three are radioactive. **Potassium** and **rubidium** have for some time been known to exhibit a small but definitely demonstrable radioactivity. It has not been found possible to explain this as due to the presence of some known radioactive substance as an impurity; it seems certain that the radioactivity of these two metals is an intrinsic property. This is especially remarkable in that the other radioactive elements are characterized by a high atomic weight, whereas the atomic weights of potassium and rubidium are relatively low.

Samarium (atomic number 62, atomic weight 150·43), an element of the rare earth group, has also been recently shown to be radioactive (HEVESY, 1933).

We can now say in recapitulation that the following well-known chemical elements are spontaneously radioactive: **uranium, thorium, samarium, rubidium** and **potassium.** To this list must be added about forty short-lived substances produced by the transformation of those just mentioned (see below).

Radioactive Transformations.—From the discovery of radioactivity onwards, the most difficult question has been that of the source of the energy of the rays emitted by radioactive bodies; for at first neither diminution of activity nor decrease of mass could be observed.

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* OTTO HÖNIGSCHMID, up to 1918 at the German Technical College in Prague, is now Professor of Analytical Chemistry at Munich.

† G. C. SCHMIDT, born 1865, at the time of the discovery at Erlangen, is now Professor of Physics at Münster.

The first step towards a recognition of the origin of radioactivity was taken by BECQUEREL, although he himself scarcely realized that his experiment would be of such a fundamental nature. BECQUEREL treated the solution of a uranium salt with excess of ammonia. Most of the original precipitate redissolved in the excess of ammonia, but a small insoluble residue remained. Having separated the two constituents by filtration, he investigated the radioactivity of each in turn. In this way he found that the soluble part was no longer active and that only the small residue, which he called **uranium-X**, exhibited radioactive properties. *On standing, however, the uranium salt recovered from the solution gradually regained the whole of its radioactivity, while the uranium-X lost its activity in the same degree.*

Soon after this RUTHERFORD * and SODDY † (1900) carried out similar experiments with the radioactive element thorium, which they likewise separated into an inactive component and an active component, called **thorium-X.** The inactive thorium regained its activity completely after some time, while the thorium-X changed anew into a number of other substances, one of which was proved with certainty to be a gas. All these new substances were radioactive. The radioactive gas discovered by these two workers was called by them **thorium emanation.**

In the same year it was found by DORN ‡ that radium also gives rise to an **emanation.** This he prepared in a manner similar to that of RUTHERFORD and SODDY for thorium emanation.

The experimental condensation of radium emanation can be conveniently carried out with the apparatus shown in fig. 3. The vessel A contains an aqueous solution of radium bromide, while the vessels B and C contain zinc blende, a substance which gives an intense fluorescence. The whole apparatus having been evacuated to a medium degree through the tap R, all three taps are closed and the vessel C is dipped into liquid air. After a time the tap between A and B is opened, whereupon the zinc sulphide in B immediately glows brightly. The tap between B and C is now also opened, and the zinc sulphide in C at once glows, while the glow in B diminishes. The tap between A and B is then closed, with the result that the glow in B vanishes completely after a short time, the emanation having condensed to a liquid in C. The tube is finally taken out of the liquid air, and the emanation vaporizes and distributes itself between B and C.

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* ERNEST RUTHERFORD (1871–1937), born at Nelson, New Zealand, studied in New Zealand and Cambridge. In 1894 he became Professor of Physics at McGill University, Montreal, in 1907 Professor at Manchester, and from 1919 was Professor of Experimental Physics and Director of the Cavendish Laboratory at Cambridge. He was knighted in 1914 and raised to the peerage as BARON RUTHERFORD OF NELSON in 1931. He carried out and directed a great deal of research in atomic physics, and received the Nobel Prize for Chemistry in 1908.

† FREDERICK SODDY, born 1877, from 1900 to 1903 occupied a position at McGill University, Montreal, where he carried out research with RUTHERFORD. He later worked with SIR WILLIAM RAMSAY. From 1904 to 1914 he held a lecturership at Glasgow, from 1914 to 1919 was Professor at Aberdeen, and later Professor of Inorganic and Physical Chemistry at Oxford.

‡ E. F. DORN (1848–1916), Professor of Physics at Halle.

If C is once more dipped into the liquid air, all the emanation returns to this part of the apparatus.

If the tap between A and B is left shut, the glow of the zinc sulphide slowly dies away, *the radioactivity of the emanation falling to half its initial value in four days.* During this time new emanation is generated in A, as can be shown by opening the tap between A and B and letting the gas flow through into the other vessels. Radium emanation (more recently called *radon*) behaves chemically as an inert gas and is therefore placed in Group O of the periodic table.

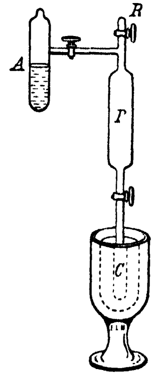

Fig. 3.—Apparatus for demonstrating the properties of radon.

The fact that radium emanation spontaneously loses its radioactivity may be explained by assuming either that the emanation itself disappears or else that it becomes transformed into a new non-radioactive substance. In order to settle this doubtful point, RAMSAY * and SODDY enclosed a small quantity of emanation, condensed by means of liquid air, in a discharge tube and examined its spectrum at regular intervals. After four days they observed spectral lines due to **helium**, which certainly had not been present originally. From this RAMSAY and SODDY deduced that the helium had been formed from the radium emanation itself. The experiment has been repeated many times, notably (in a modified form) by RUTHERFORD (p. 17), and RAMSAY'S conclusion has been established beyond question.

From all these experiments it follows with certainty that *the emission of rays by a radioactive body is accompanied by a transformation of the matter of which the body is composed.*

RUTHERFORD was the first to recognize this transformation as the origin of radioactive phenomena. According to his view, which is now firmly established on the basis of experiment, the atoms of a radioactive element are disintegrating continuously, and it is this disintegration that provides the energy for the rays emitted.

Further Transformations of Radioactive Substances.—Radium is continuously emitting rays and at the same time generating radium emanation (the inert gas *radon*). As a rule this radon does not completely escape from the solid radium salt, but remains occluded in it to a great extent. The radon then disintegrates further; we have already seen that it gives rise to helium.

Helium, however, is only one of the resulting products. It is found that any substance which comes into contact with the emanation, itself becomes "infected", as it were, with radioactive properties. This leads us to assume that the gaseous radon itself breaks down further, giving rise to a solid which is deposited on bodies brought into contact with the radon.

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* Sir WILLIAM RAMSAY (1852–1916) was born in Glasgow. From 1872 onwards he occupied academic positions in Glasgow, in 1880 was appointed to the chair of Chemistry at Bristol, and in 1887 became Professor at University College, London, a position which he held until his resignation in 1913. He was awarded the Nobel Prize for Chemistry in 1904. His researches cover a wide field, including the chemistry of alkaloids and the vapour pressure and surface tension of liquids. He also, in association with Lord Rayleigh, discovered argon and other rare gases in the atmosphere.

It has been found possible to concentrate this active solid by introducing into the vessel containing the radon a wire which is kept at a negative potential of several hundred volts relative to the rest of the vessel. The radioactive product, which is known as *radium A*, is then deposited mainly upon the wire. Radium A in turn gives rise to further disintegration products, called RaB, RaC, . . . , RaF in order.

The various products are to a great extent retained (occluded) in the original radium salt, and hence the rays emitted consist of those due to radium itself together with those of all its disintegration products. This naturally introduces very great difficulties into the investigation of the properties of radium and the substances produced from it by disintegration, unless it is possible to separate these products from radium and from one another.

Radon can be separated completely from the parent radium salt by dissolving the salt in water and boiling the solution for a long time. In this way the gaseous radon is all boiled off, and the residual solution contains the radium salt together with the later disintegration products RaA, RaB, and RaC. (The subsequent products are of minor importance in this connexion, as their radioactivity is feeble in comparison with that of radium itself). RaA, RaB, and RaC, however, have very short life-periods, and after about four hours only a negligible quantity of them remains. Subsequently, therefore, the solution emits practically nothing but the rays due to radium.

4. The Rays emitted by Radioactive Elements

Complex Nature of the Rays.—For the purpose of investigating their rays, radioactive substances are placed in small boxes made of vulcanite or lead and provided with a very thin mica window. If the walls of the box are thick and made of lead, they absorb the rays falling upon them, so that rays cannot escape except by passing through the thin mica window.

In fig. 4 B represents a lead box containing a small quantity of radium bromide or chloride. Out through the window in the top of the box there passes a narrow beam of nearly parallel rays. The application of a magnetic field with its lines of force perpendicular to the plane of the figure in the direction away from the reader causes the beam to split up into three quite distinct parts. This may be proved experimentally by means of photographic plates in suitable positions. The three different kinds of rays are called **α-rays, β-rays,** and **γ-rays.** The α-rays are deflected by the magnetic field very slightly to the left in the figure, the β-rays are deflected strongly to the right, while the γ-rays are not deflected at all, but continue in a straight line.

The deflection of the *α-rays* is consistent with the view that they form a current of positive electricity. Thus their behaviour in the magnetic field is similar to that of *canal rays* (*positive rays*). The *β-rays*, like *cathode rays*, are deflected like a current of negative electricity. The *γ-rays* behave in general like extremely hard *X-rays*; for instance, they can pass to a considerable extent even through fairly thick plates of lead and steel. Corresponding differences in the behaviour of α-, β- and γ-rays can also be observed in other circumstances, e.g. in an electrostatic field.

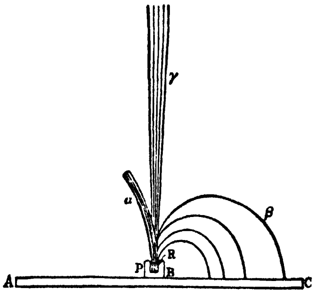

Fig. 4.—The effect of a magnetic field perpendicular to the plane of the figure upon the different types of rays emitted by radioactive substances.

The penetrating power of α-rays is only very slight: they are actually stopped completely by a thin sheet of paper. Under the same conditions β-rays are absorbed to a much smaller extent, while γ-rays are not appreciably affected at all. Correspondingly, the distances travelled by the different kinds of rays in air (their so-called *ranges in air*) are very different (p. 18). In passing through a gas the rays give rise to carriers of electricity (ions), a fact which makes it possible to observe their tracks in a Wilson cloud-chamber. The cloud-tracks of the different kinds of rays can readily be distinguished from one another (cf. Vol. III, p. 337, and this volume, p. 19). See further p. 37.

Scintillation.—If a small quantity of a radioactive substance is placed at a short distance from a fluorescent zinc blende screen and the screen is then examined with a lens, an irregular flashing of tiny individual sparks is observed. Crookes,* who was the first to describe these flashes (March, 1903 †), called them **scintillations.** The scintillations produced by α-rays are especially brilliant. The fact that the effect is made up of separate and distinct flashes indicates that the α-rays themselves consist of a stream of separate and distinct particles (α-particles). The scintillations produced by β-rays are much feebler and scarcely recognizable as individual flashes. Finally, γ-rays give no scintillations, but only a continuous glow on the screen. All three kinds of rays also affect a photographic plate.

α-Rays.—Information as to the nature of α-rays is obtained by quantitative investigation of their deflection in electric and magnetic fields, as explained in Vol. III, p. 314 *et seq.* A Wilson cloud-track photograph showing the magnetic deflection of α-rays is reproduced in Vol. III, fig. 55, p. 337. The method of superimposed electric and magnetic fields gives one and the same value of e/m for the α-rays from the most widely different radioactive substances. This value is $4{\cdot}8 \times 10^4$ coulombs per gramme. Comparison with the value of e/m obtained for the proton (Vol. III, p. 346) shows that the α-ray value is just half the proton value. From this we conclude that the α-particle either has mass 2 and a single elementary charge or else has mass 4 and two elementary charges. In order to settle which of these two alternatives is correct, it was necessary to determine either e or m independently.

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* Sir William Crookes (1832–1919), at first professor at the Training College at Chester, later for many years President of the Society of Chemical Industry. See also footnote, Vol. III, p. 328.

† They had previously been investigated in detail by Elster and Geitel.

The direct measurement of e for α-particles was made in 1908 by Rutherford and Geiger and by Regener.* The last-named had shown earlier that practically every α-particle which strikes a properly prepared phosphorescent screen of zinc sulphide causes a flash of light. He was thus able to find the time average of the number of particles falling upon a given area simply by counting the flashes, while the charge carried by this number of α-particles could be determined separately.

Fig. 5.—Record of α-particles obtained from a Geiger counter

Geiger originated another and more reliable method of counting α-particles. This is by means of the Geiger counter (Vol. III, p. 350), which consists of a cylindrical condenser with a wire for the inner central electrode. Between the electrodes a potential slightly lower than that required to produce a discharge through the air dielectric is applied. The rays under investigation enter the counter through a window of thin foil. Every time an α-particle enters and renders the air conducting there is a sudden brief discharge, which can be observed by means of an electrometer. The number of these brief discharges is equal to the number of α-particles passing into the counter.

Fig. 5 shows a photographic record, taken upon a moving film, of the electrometer " kicks " caused by the entry of α-particles into a counter. The upper record was taken with a rate of entry of 600 α-particles per minute, the lower record with 900 per minute. The film was moved past the recording instrument at a speed of about 150 cm. per minute. A few of the deflections are clearly seen to have twice the normal amplitude. These correspond to the entry of two α-particles almost at the same instant.

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* Erich Regener became Professor at Berlin in 1914, and in 1920 went to the Technical College at Stuttgart.

By the above methods it was found possible to determine the magnitude of the positive charge on a single α-particle. The value obtained is twice that of the charge on an electron, i.e. $2 \times 1{\cdot}59 \times 10^{-19}$ coulombs.

From this it follows that we are dealing with particles with a double positive charge and mass 4. But this is the atomic weight of helium; hence α-particles must be doubly charged helium atoms, i.e. He^{++}. If this is so, then helium must be produced in the neighbourhood of a radioactive substance emitting α-rays. This is exactly what RAMSAY and SODDY actually observed (p. 13). The production of helium was also demonstrated by RUTHERFORD in the following way.

A minute quantity of radium was sealed up in a small glass tube with extremely thin walls, so thin that the α-rays emitted could pass out, although the emanation simultaneously formed was held in. This small glass tube was enclosed in another tube provided with electrodes, and the spectrum produced on passing a discharge was observed at regular intervals. It was found that after a few days the spectral lines of helium made their appearance. This proves that helium is produced from the α-rays. The fact that helium is always found present in radioactive minerals is also evidence that it is a product of radioactivity (p. 32).

Thus α-rays consist of helium atoms with a double positive charge, shot with great velocity out of the atoms of radioactive substances.

Range.—Investigation of the way in which the intensity of the α-rays falls off with increasing distance from a radium preparation gives a surprising result. It is found that all trace of the rays (such as ionization or scintillation) suddenly stops at the very accurately measurable distance of 3·30 cm. in air at normal pressure. This distance is known as the *range* of the α-rays from radium in air. The α-rays from other radioactive elements have different ranges. Thus the α-rays emitted by radon can be observed up to a range of 4·16 cm. in air at normal pressure, but beyond this distance no trace of them can be observed. As was discovered by GEIGER, the range R bears a simple relationship to the velocity v_0 with which the α-particle under consideration leaves the parent atom. This relationship may be written in the form

$$v_0^3 = a\mathrm{R},$$

where a is a constant whose value may be computed from the accurate data $v_0 = 1{\cdot}92 \times 10^9$ cm. per second and $\mathrm{R} = 6{\cdot}97$ cm. for RaC′ (see p. 79). The definite and unique character of the range is shown

TABLE III.—THE RADIOACTIVE SUBSTANCES

Substance	Z	Rays emitted	Half-life Period	v in cm./sec. × 10⁹	Range in cm. 15° C.	Atomic Weight
Uranium I	92	α	4·5 × 10⁹ yr.	1·40	2·70	238·18
Uranium X₁	90	β	23·8 days	14·4–17·7	—	234
99·65 % ↓ β β↓ 0·35 %						
Uranium Z	91	β	6·7 hours	—	—	—
Uranium X₂ ↓ β	91	β, γ	70 seconds	24·6–28·8	—	234
Uranium II	92	α	about 10⁶ yr.	1·50	3·28	234
$\xrightarrow[3\%]{\alpha}$ UrY	90	β	24·6 hours	—	—	230
97 % ↓ α						
Ionium	90	α	about 9 × 10⁴ years	1·48	3·03	230
Radium	88	α (+ β, γ)	1580 years	1·51	3·38	226·0
Radium emanation (Radon)	86	α	3·83 days	1·61	4·12	222
Radium A ..	84	α	3·0 minutes	1·69	4·72	218
Radium B .. β	82	β + γ	26·8 minutes	10·8–24·1	—	214
Radium C ..	83	α + β (+ γ)	19·6 minutes	1·6	4	214
α↓ 0·03 %						
99·97 % ↓ β Radium C″	81	β + γ	1·32 minutes	—	—	210
Radium C′ ↓	84	α	0·9 × 10⁻⁸ sec.	1·92	6.97	214
Radium D (Radio-lead)	82	β + γ	16 years	9·9–12·1	—	210
Radium E ..	83	β + γ	4·85 days	∼ 23·1	—	210
Radium F (Polonium)	84	α (+ β)	136·5 days	1·59	3·92	210
Radium G (Uranium lead)	82	—	∞	—	—	206·0
Proto-actinium← – – – –	91	α	1·2 × 10⁴ yr.	1·55	3·68	231 ± 1
Actinium	89	β	about 20 yr.	—	—	227 ± 1
Radio-actinium	90	α (+ β + γ)	18·9 days	1·68	4·68	227 ± 1
Actinium X	88	α	abt. 11·2 days	1·65	4·41	223 ± 1
Actinium emanation ..	86	α	3·9 seconds	1·81	5·79	219 ± 1
Actinium A	84	α	0·0015 sec.	1·89	6·58	215 ± 1
Actinium B	82	β + γ	36·0 minutes	11·4–19·5	–	211 ± 1
Actinium C	83	α + β	2·16 minutes	1·78	5·51	– –
β↓ 0·32 %						
99·68 % ↓ α Actinium C′ ..	84	α	abt. 0·005 sec.	18–27·3	6·49	211
Actinium C″ ↓ ..	81	β + γ	4·76 minutes		—	207 ± 1
Actinium D (Actinium lead)	82	—	∞ (?)		—	207 ± 1
Thorium	90	α	1·65 × 10¹⁰ yr.	1·39	2·59	232·12
Mesothorium I	88	β	6·7 years	—	—	228
Mesothorium II	89	β + γ	5·95 hours	11–29·97	—	228
Radiothorium	90	α (+ β)	1·90 years	1·60	4·01	228
Thorium X	88	α	3·64 days	1·64	4·25	224
Thorium emanation ..	86	α	54·5 seconds	1·73	5·06	220
Thorium A	84	α	0·14 seconds	1·80	5·68	216
Thorium B	82	β + γ	10·6 hours	18–23·1	—	212
Thorium C	83	α + β	60 minutes	1·7	4·79	212
β↓ 65 %						
35 % ↓ α Thorium C′ ..	84	α	abt. 10⁻¹¹ sec.	2·06	8·62	212
Thorium C″ ↓ ..	81	β + γ	3·20 minutes	8·7–25·2	—	208
Thorium D (lead) ..	82	—	∞		—	208

very elegantly by cloud-track photographs (see, e.g., fig. 6). Towards the end of their range α-particles capture first one electron and then a second, thus becoming ordinary neutral helium atoms. A number of α-ray ranges are given in Table III.

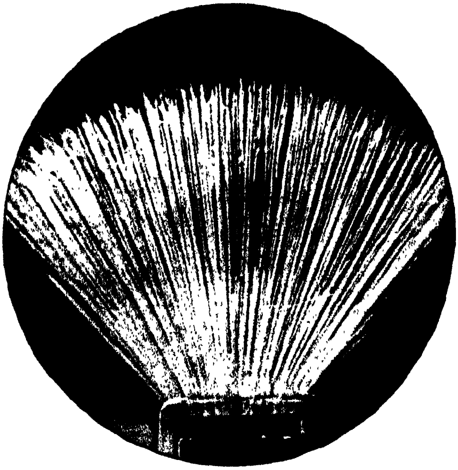


Fig. 6.—Cloud-track photograph showing definite ranges of α-rays. The radioactive preparation contains two active elements ThC and ThC′. The two definite α-ray ranges are clearly visible.

[From Meitner, *Atomvorgänge und ihre Sichtbarmachung* (F. Enke, Stuttgart).]

Note.—Experiments in which α-particles are counted by the scintillation method or with a Geiger counter have a special significance in that they provide convincing evidence in favour of the atomic theory of matter. This is true in even greater degree of the observation of the tracks of single α-particles in the Wilson cloud-chamber. In the individual scintillations, the individual electrometer " kicks ", and the individual cloud-tracks we see the effects of individual α-particles. Previous to this only the total effects of enormous numbers of atoms acting simultaneously had been observed in physics and chemistry, and the existence of individual atoms had been postulated on purely theoretical grounds. The opponents of the atomic theory always used to object that no one would ever be able to observe atoms one by one, and even the most enthusiastic supporters of the theory never expected such a thing to be possible. This state of affairs was revolutionized by the experimental counting of α-particles (charged helium atoms). The atomic theory now has a basis of experimental observation, and the results obtained in counting experiments are completely in accordance with expectations. (See, however, Chapter IV, p. 256.)

β-Rays.—Determinations of e/m for β-rays have given the values quoted in Vol. III, p. 322. Taking account of the change of mass with velocity, we have $e/m_0 = 1{\cdot}77 \times 10^8$ coulombs per gramme.

Hence β-rays consist of very rapidly moving electrons and are essentially the same as fast cathode rays.

As with α-rays, the β-rays from different substances have different energies.

The velocity of the β-rays emitted by ThC is about 0·96 c (c being the velocity of light), of those from RaE about 0·94 c, and of those from UX_1 about 0·6 c. These are mean values; for it is found that the velocities of the β-rays from any given radioactive disintegration are not all the same, but vary continuously from zero up to high values (see fig. 7, which gives the distribution curves for various substances). Thus in contrast to the α-particles, the β-particles from any given process are not associated with a definite energy.

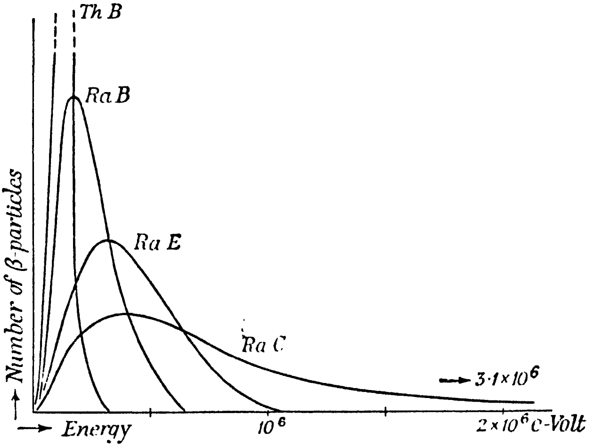


Fig. 7.—Energy distribution of primary β-rays

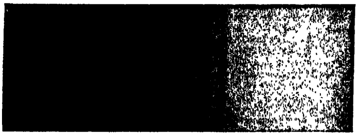


Fig. 8.—Magnetic velocity-spectrum of β-rays. Part of the spectrum of ThB + ThC.

[From *Handbuch der Physik*, Vol. XXII, Part I (Springer, Berlin).]

Apart from these β-rays which form a direct accompaniment of certain radioactive transformations (so-called *primary* β-rays), another class of β-rays (so-called *secondary* β-rays) are observed in all transformations in which γ-rays are emitted. The secondary β-rays have widely varying, but generally quite definite velocities, and derive their energy from the γ-rays. Fig. 8 shows a magnetic spectrum of secondary β-rays, i.e. a record obtained with apparatus identical in principle with that of fig. 4, p. 15, if we imagine a photographic plate placed on the right and the source to have a linear form. The emission of secondary β-rays is explicable as a kind of photoelectric effect (p. 133). The rays consist of electrons which have received energy from the γ-rays of the radioactive process (see further p. 358). L. MEITNER succeeded in producing these secondary β-rays artificially from platinum and lead by the action of the γ-rays of ThB.

The fastest β-rays observed from any known radioactive substance are those at the upper energy limit of the β-rays from RaC. Their velocity is 99 per cent of that of light. To reach this velocity an electron would have to pass through a potential drop of 3·15 million volts.

γ-Rays.—These consist of electromagnetic waves and hence are not deflected by electric or magnetic fields. They are therefore similar in character to light and X-rays, from which they differ only in their much shorter wave-length. This has been verified by direct measurements with gratings (p. 72), the gratings consisting of the lattice planes of crystals and the grating constant being the distance between these planes (compare Vol. I, p. 274). An example of a grating spectrum of γ-rays is given in fig. 9.

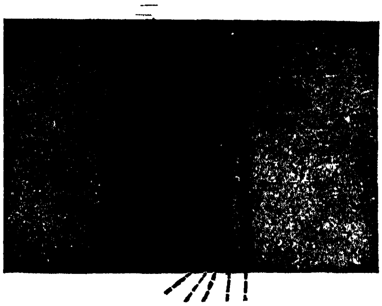


Fig. 9.—Spectrum of γ-rays obtained by reflection from the grating formed by a crystal of rock-salt; glancing angle 10′ (after Frilley).

[From Rutherford, *Radiations from Radioactive Substances* (Cambridge University Press).]

By a kind of photoelectric effect (p. 133) γ-rays produce from the disintegrated atoms the secondary β-rays referred to above. From the energy of these secondary β-rays it is possible to calculate the wave-lengths of the corresponding γ-rays by means of an equation which will be given later (pp. 134, 359).

The γ-ray spectra, like optical line spectra, consist of a number of sharply defined monochromatic lines. The wave-lengths lie between 300 and about 2 X-units (1 X-unit = 10^{-11} cm.). Thus γ-rays bear somewhat the same relationship to ordinary light waves as ordinary light waves bear to short radio waves. L. MEITNER succeeded in showing from the energy of the secondary β-rays from radioactinium and actinium X that the emission of γ-rays does not occur until *after* the disintegration of the atom. Thus we are led to the conclusion that γ-rays are emitted in the process of rearrangement of the atom into a stable form after the radioactive disruption. Such an emission of γ-rays does not, however, follow every α- or β-ray change; certain atoms are known to disintegrate without emitting γ-rays.

5. Radioactive Series

Sequence of Transformations.—In the light of what has been said above it can be seen that radioactivity consists in the spontaneous disintegration of atoms (usually of high atomic weight) with expulsion of charged helium atoms (α-particles) or electrons, the atoms thereby being transformed into new atoms with different chemical properties. For the most part the new atoms produced are not stable, but in turn disintegrate more or less rapidly. In this way we get a whole sequence of disintegrations or so-called radioactive series.

The most important is the *uranium-radium series.* It is a remarkable fact that uranium minerals derived from the most widely different sources always contain radium in the same relative amount. According to W. MARCKWALD (1913), $3{\cdot}3 \times 10^{-7}$ gm. of radium is always associated with 1 gm. of uranium. This forces us to the conclusion that the radium has been produced from the uranium, i.e. is a disintegration product of uranium. The atomic weight of uranium, as determined by HÖNIGSCHMID, is $238{\cdot}17 \pm 0{\cdot}007$, i.e. is 12 greater than that of radium. Hence in the sequence of transformations by which radium is produced from uranium the number of α-particles (each of mass 4) expelled must be three. We accordingly deduce that between uranium and radium there must be two further substances which emit α-rays. These have actually been discovered (see Table III). Each radium atom disintegrates into a negatively charged radon atom and a positively charged helium atom. The latter is shot out as an α-particle and eventually becomes an ordinary helium atom by neutralization of its charge.

The radon atom expels another α-particle (which is eventually neutralized and becomes helium) and is itself transformed into an atom of radium A. This substance is a solid which, as mentioned above (p. 14), deposits itself as an invisible film upon the walls of the containing vessel or other solids, thus giving rise to so-called induced radioactivity. Then in a short time the radium A is transformed into radium B with expulsion of α-particles, and the radium B is in turn transformed into radium C with expulsion of β-particles. Radium C emits rays of all three kinds. Careful investigations have shown that its mode of disintegration is rather complicated, for it gives rise simultaneously to two new substances. A very small fraction of the radium C (only 0·03 per cent) is transformed by an α-ray change into RaC″. The remainder (i.e. 99·97 per cent) passes into RaC′ with emission of β-rays. Both RaC′ and RaC″ give rise to the same product RaD, the former by expelling α-particles and the latter by expelling β-particles. RaD is then transformed by a β-ray change into RaE, which in turn emits both β- and γ-rays and becomes RaF, a substance which has been identified with polonium. Finally, RaF is transformed with emission of α-rays into RaG. This last product is regarded as chemically identical with lead, although so far it has not been found actually possible to detect by chemical means the lead formed in an experiment. Such radioactively-produced lead, which is distinguished by an atomic weight differing from that of ordinary lead, however, has been detected in minerals (p. 27).

In addition to the uranium-radium series there are also the *actinium series* and the *thorium series.* As may be seen from Table III, all these series exhibit remarkable similarities.

The Law of Radioactive Disintegration.—Radioactive change takes place in such a way that in each unit of time the same fraction of the substance present at that time undergoes disintegration. Thus if the amount of substance (i.e. the number of atoms) left unchanged at time t is N, and the amount disintegrating during the element of time dt is $d\mathrm{N}$, the quotient dn/N is proportional to dt. We may accordingly write

$$\frac{d\mathrm{N}}{\mathrm{N}} = -\lambda\, dt,$$

in which λ is a constant and the minus sign is chosen because N decreases as t increases. Integrating this equation, we obtain

$$\log_e \mathrm{N} = -\lambda t + \text{constant}.$$

Now suppose that $\mathrm{N} = \mathrm{N}_0$ when $t = 0$. It follows that the constant of integration is equal to $\log_e \mathrm{N}_0$. Substituting this value in the integrated equation and rewriting it, we have

$$\mathrm{N} = \mathrm{N}_0 e^{-\lambda t}.$$

The constant λ is called the **radioactive constant** or **decay constant** of the substance under consideration. It is a measure of the specific intensity of the radioactivity. The quantity $1/\lambda$ is usually called the **mean life period.**

The rate of disintegration of a radioactive substance is usually given by means of the so-called **half-life period,** i.e. the time required for half the original quantity to be transformed. Calling this time T, we have

$$\tfrac{1}{2}\mathrm{N}_0 = \mathrm{N}_0 e^{-\lambda \mathrm{T}},$$

whence

$$\mathrm{T} = \frac{1}{\lambda}\log_e 2 = \frac{0{\cdot}693}{\lambda}.$$

This result expresses the relation between the radioactive constant λ and the half-life period T.

The half-life period has a characteristic constant value for each radioactive element, differing very widely in different cases. It enables us to distinguish between the different members of a series, e.g. the various disintegration products mentioned above.

The Geiger-Nuttall Relationship.—There is an interesting relationship between the decay constant λ for any element and the velocity v or range R of the α-particles which it emits. (See fig. 10.) To a first approximation it is found that

$$\log \lambda = A + C \log R,$$

where A and C are constants; or, since R is proportional to v^3,

$$\log \lambda = A + B \log v.$$

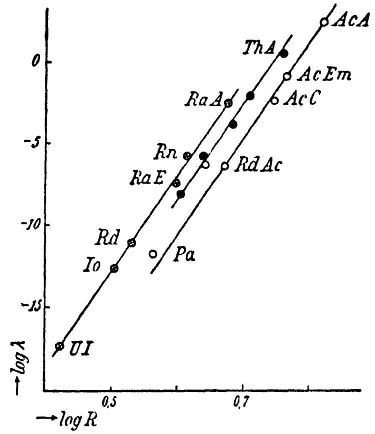


Fig. 10.—Relation between decay constant and range of emitted α-particles

Elements indicated by dots, reading upwards: RdTh, ThX, ThC, ThEm, ThA.

The point shown as a circle close to ThX represents AcX.

Fig. 11 brings out the physical significance of the Geiger-Nuttall relationship more clearly than fig. 10, in that it graphically represents the relationship between the logarithm of the decay constant and the energy of the α-particles.

We see that the shorter the life of the element under consideration, the greater is the energy (or velocity or range) of the α-particles it expels. For an interpretation of this relationship see p. 358.

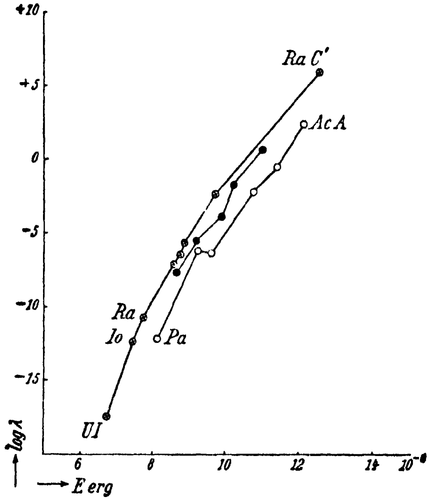
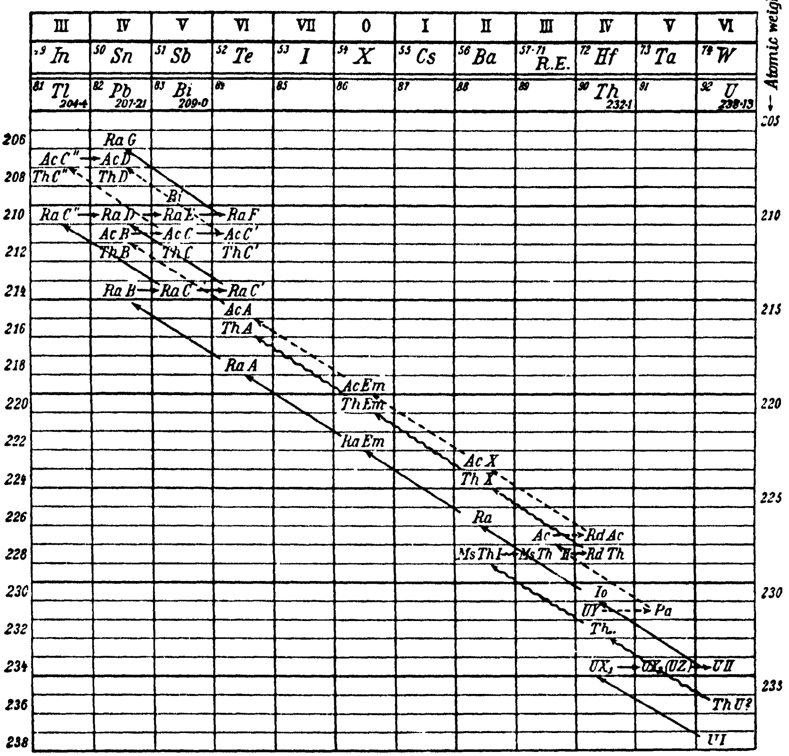


Fig. 11.—Relation between decay constant and energy (after Gamow)

TABLE IV.—RELATIVE POSITIONS OF THE RADIOACTIVE ELEMENTS IN THE PERIODIC TABLE



α-ray change = decrease of atomic weight by 4 units and displacement of 2 places to the left (i.e. decrease of the atomic number by 2).

β-ray change = no change of atomic weight and displacement of 1 place to the right (i.e. increase of atomic number by 1).

⟶ = uranium series.

··· ⟶ = actinium series.

⤳ = thorium series.

For the sake of clearness the thorium series is only shown as far as ThA; beyond that point it runs parallel to the actinium series, but with atomic weights less by 1.

Radioactive Disintegration and the Periodic Table.—Remarkable regularities are observed in the chemical properties of the members of a radioactive series. Each time an α-particle is emitted the valency of the atom alters by two units in the sense corresponding to a decrease of atomic number. Each time a β-particle is emitted, on the other hand, the valency alters by one unit in the opposite sense. In Table IV a portion of the end of the periodic table (Table I) is reproduced, the table being arranged so that the inert gases are in the middle. The radioactive elements are represented by means of a modification of the usual scheme, in which atomic weights are taken as ordinates and valencies (or more correctly, atomic numbers) as abscissæ. From this scheme we can deduce the so-called *displacement rule*, first enunciated by SODDY and FAJANS (1913):

The emission of an α-particle causes a decrease of two in the atomic number, i.e. a displacement of two places to the left in the periodic table. The emission of a β-particle causes an increase of one in the atomic number, i.e. a displacement of one place to the right in the periodic table.

Accordingly we see, e.g., that U I is transformed by three successive disintegrations (α, β, β) into U II, an element situated in the same group as U I and with the same atomic number 92. It follows that the two elements U I and U II must be entirely identical in all their chemical properties, and in actual fact it is quite impossible to separate these two elements from one another by chemical means. From a chemical point of view the mixture constitutes but one element. Other cases exhibit the same complexity in a more striking way. Thus the end-product of the uranium series is an element with the atomic number (and hence also all the chemical properties) of lead. From the known atomic weight of uranium and from the successive stages of the disintegration series we can deduce that this end-product must have the atomic weight 206, as compared with 207·180 for ordinary lead. In the same way ThD must be chemically identical with lead, but must have the atomic weight 208. Accordingly, a number of chemically identical leads with different atomic weights must exist.

In 1914 HÖNIGSCHMID prepared pure lead from an African pitchblende which was free from thorium and contained exceptionally small amounts of other metals as impurities. He then determined its atomic weight, using the same methods and reagents as in the experiments by which he had previously found the atomic weight of ordinary lead to be 207·180. For the lead from pitchblende he obtained the value 206·046. This makes it certain that the lead in pitchblende is almost entirely a disintegration product from uranium. The accuracy of the determinations is much greater than the observed difference, which has been confirmed by other workers. Later (1917), HÖNIGSCHMID also investigated lead from thorite and thorianite. As was expected, the nearly pure thorium-lead gave a very high atomic weight, namely 207·90.

Such chemically identical and chemically inseparable elements with different atomic weights are called isotopes.*

As may be seen from Table IV, further groups of isotopes are thorium, radiothorium, ionium, uranium X, and uranium Y; mesothorium, thorium X, and radium; radium B, radium D, and the various isotopes of lead; and finally radium F (polonium), radium A, radium C′, thorium A, and thorium C′. Radium D, being chemically undistinguishable from ordinary lead, was at first called radio-lead. The actinium derivatives are also isotopic with the corresponding radium derivatives. Only in their different life-periods (and of course in their atomic weights) do the radioactive isotopes differ from one another.

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* Gr. *isos*, equal, *topos*, place. Whole families of isotopes are sometimes called *pleiads*.

The line spectra of RaG (atomic weight 206) and ordinary lead (207·18) are practically identical in the visible and ultra-violet regions, though very accurate interferometric measurements have shown the existence of small differences (a few hundredths of an Ångström).

Appreciable differences in density have also been found (compare p. 95). Thus T. W. Richards and C. Wadsworth obtained the value 11·337 for ordinary lead (atomic weight 207·2), but 11·288 for a mixture of RaG and Pb (atomic weight 206·3). The densities are such that the quotient of the atomic weight and the density (the so-called atomic volume) is constant — in this case 18·28. Since isotopic atoms differ in mass, it must be possible to separate isotopes by processes depending on mass. Such experiments have, in fact, been carried out successfully (p. 96).

6. The Energy of Radioactive Changes

Radioactive Equilibrium.—As a rule the radioactive products from a solid salt remain occluded in it, so that the mixture emits all three types of rays with intensities corresponding to the amounts of the components. This explains why a freshly recrystallized radium salt shows little activity; in this pure state it emits only its own proper α-rays. Gradually, however, the observed activity increases as the more active products accumulate. Eventually a maximum value is reached, when the quantities of the products formed in any given time become equal to the quantities which disappear as a result of disintegration. Under these conditions a state of equilibrium is attained. The amount of each product tends to be diminished by its own disintegration and increased by the disintegration of its parent substance. When radioactive equilibrium is reached these two tendencies are equal, i.e. the rate of disintegration of each product is equal to the rate at which it is formed, i.e. equal to the rate at which its parent substance disintegrates. This holds throughout the series. Let the quantities (i.e. numbers of atoms) of the different substances present be respectively $N_1, N_2, N_3, \ldots$ and their decay constants $\lambda_1, \lambda_2, \lambda_3, \ldots$; then when equilibrium is reached

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} = \ldots = -\lambda_1 N_1 = -\lambda_2 N_2 = -\lambda_3 N_3 = \ldots .$$

That is: *in radioactive equilibrium the amounts of the different substances* *in the equilibrium mixture are inversely proportional to their respective decay constants or directly proportional to their respective half-life periods.*

As an example of the application of this result, we may take the calculation of the half-life period of uranium from the known half-life period of radium (1580 years) and the observed radium : uranium ratio ($3{\cdot}5 \times 10^{-7}$) in minerals. Writing T for the half-life period, we obtain

$$T_{Ra} : T_{U} = 1580 : T_{U} = 3{\cdot}5 \times 10^{-7}$$

whence

$$T_{U} = \frac{1580}{3{\cdot}5 \times 10^{-7}} = 4{\cdot}5 \times 10^{9} \text{ (years).}$$

This value applies to U I, since the quantity of U II is relatively negligible.

Since the rate of disintegration is the same for all the members of a series present when radioactive equilibrium is reached, it follows that the total rate of emission of α-particles from the mixture must be greater than that from the pure parent substance by a factor equal to the number of members which emit α-rays. Over times comparable with the life-period of the parent substance the total activity is observed to fall off as a consequence of the progressive disintegration of the parent. Hence after a certain time the total observed activity passes through a maximum of intensity. The observation of this point has an important bearing on the determination of the life-periods and the number of products emitting α-rays.

Evolution of Heat.—We consider a quantity of a radium salt sealed up in a small glass tube with walls of such a thickness that only the penetrating β- and γ-rays can pass out, the α-rays being held back. The β-rays carry away negative electricity, and the radium salt left behind must therefore become positively charged. The disappearance of this positive charge has actually been observed in the form of a powerful spark when a tube of this kind was opened.

The β-rays emitted by the salt consist (as we have seen) of negative electrons of small mass, which are able to pass through the walls of the containing tube. The relatively massive α-rays, on the other hand, are stopped by the walls and give up their kinetic energy. The α-particles impinge upon the walls and in the process their energy is transformed into heat, with the result that the temperature of the radium salt rises. It is actually found that the temperature of radium salts is several degrees higher than that of their surroundings.

Of course this heating effect represents only a fraction of the energy given out by the radium. Recent measurements show that the rate of evolution of energy from radium is 140 cal. per hour per gramme. One kilogram of radium would evolve 140 k.cal. per hour, i.e. about a million k.cal. per year. To obtain this amount of energy it would be necessary to burn about 130 kgm. of the best coal. The energy evolved from 1 kgm. of radium would drive a machine of about $\frac{1}{8}$ horse-power continuously (although of course the power would fall off by half in 1580 years). The total energy evolved by 1 gm. of radium before disappearing entirely would be $3{\cdot}7 \times 10^9$ cal., i.e. a million times more than that furnished by the combination of sufficient hydrogen and oxygen to form 1 kgm. of water. The amount of heat evolved by other radioactive elements, such as thorium and uranium, has also been measured. Since the rate of disintegration of uranium is slow, so also is the rate of heat production. It is found that 1 gm. of uranium in equilibrium with its disintegration products evolves about $2{\cdot}5 \times 10^{-8}$ cal. per second. The corresponding figure for thorium is $6{\cdot}8 \times 10^{-9}$ cal. per second.

Number of α-Particles Emitted.—The best direct determinations by counting give $3{\cdot}72 \times 10^{10}$ α-particles per second per gramme of radium (HESS and LAWSON). In radioactive equilibrium each gramme of radium gives four times this number per second ($15{\cdot}7 \times 10^{10}$); for the total observed includes, in addition to the α-particles from Ra itself, those from RaEm, RaA and RaC.*

The results of these counting experiments may be used to calculate the Avogadro constant (Vol. II, p. 52), the method being completely independent of the kinetic theory of gases. According to p. 23, we have

$$N = -\frac{dN}{dt} \cdot \frac{1}{\lambda},$$

where N is the number of radioactive atoms remaining at a given time t. By actual counting we find that for 1 gm. of radium $dN/dt = -3{\cdot}72 \times 10^{10}$. From p. 23 we have further

$$\frac{1}{\lambda} = \frac{T}{\log_e 2} = \frac{1580 \text{ years}}{0{\cdot}693} = \frac{1580 \times 365 \times 86400}{0{\cdot}693} = 7{\cdot}18 \times 10^{10} \text{ sec.}$$

As the atomic weight of radium is 226, the number of atoms in a gramme-atom (i.e. in 226 gm.) is

$$N = 7{\cdot}18 \times 10^{10} \times 3{\cdot}72 \times 10^{10} \times 226 = 6{\cdot}05 \times 10^{23}.$$

In most radioactive investigations, as a matter of fact, the calculation is reversed.

There is still another way of deriving the Avogadro number. As was first found experimentally by DEWAR in 1910, the volume of helium generated by 1 gm. of radium per year is 164 mm.³. In radioactive equilibrium the number of α-particles emitted is four times that from radium alone, i.e.

$$3{\cdot}72 \times 10^{10} \times 4 \times 365 \times 86400 = 4{\cdot}69 \times 10^{18}.$$

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* The α-ray contribution of RaC′ is negligible. It is further assumed that, on account of its very long life-period, radioactive equilibrium has not yet been attained for RaD.

On the assumption that each α-particle gives one helium atom, the number of helium atoms contained in 1 cm.^{3} is

$$\frac{469 \times 10^{16}}{0{\cdot}164} = 2{\cdot}86 \times 10^{19},$$

so that the number per gramme-atom comes out as $6{\cdot}4 \times 10^{23}$. This is quite a good value for the Avogadro constant.

Number of β-Particles Emitted.—This is very difficult to determine with certainty. A large number of different experiments have given the result that in all probability one β-particle (electron) is expelled per atom in β-ray disintegration. On account of the continuous energy distribution of β-rays (see fig. 7, p. 20) this result is very important in connexion with the theory of β-ray disintegration (p. 359).

7. The Geological Significance of Radioactivity

Distribution of Radioactive Substances.—In the course of their investigations Elster and Geitel observed that the air in subterranean spaces, such as mines and cellars, possessed a remarkably high conductivity. The same is true of air sucked up out of the earth by means of a tube driven down into the ground. In both cases the ionization of the air gradually dies away over a number of days, the observed half-life period being about four days. This behaviour is consistent with the explanation that a certain quantity of radium emanation is mixed with the air, and we are thus led to the conclusion that the earth's crust as a rule contains radium.

This conclusion can be tested by making use of the fact that the disintegration products of radium emanation are deposited upon negatively charged bodies. A conductor (most conveniently a wire) is suspended on insulating supports in a subterranean space and is maintained for several hours at a potential of about −2000 volts. After this " exposure " the wire is found to have become radioactive on account of the radium A, B, and C deposited upon it. The coating of active substances may be removed by rubbing the wire with a soft leather and may then be tested for radioactive properties by the usual methods (production of conductivity in the air, scintillations on a zinc blende screen, blackening of a photographic plate). A negatively charged wire hung up even in the open air shows the same behaviour.

The active deposit proves on closer examination to be a mixture of the disintegration products of radium emanation and thorium emanation.

Both radium and thorium can actually be detected in all kinds of *soil and rock.* Primary rocks contain on an average 2×10^{-12} gm. of radium (or 6×10^{-6} gm. uranium) per gramme. Their thorium content is about 2×10^{-5} gm. per gramme. The content of radium and thorium in sedimentary rocks is very variable, being greatest in clays and least in limestone and sandstone.

It is to be assumed that the radium has always originated from a corresponding uranium content. In many cases it has been possible actually to detect the presence of uranium, although the chemical tests are relatively insensitive and difficult to carry out.

Like the air contained in the earth, all *water* in contact with the earth contains radium emanation. Many hot springs are particularly rich in it, and the sinter from them contains radium compounds, sometimes in concentrations high enough for commercial exploitation.

Evolution of Heat in the Earth by Radioactive Substances.—The energy given out by the radioactive substances distributed through the soil and rocks plays a part in maintaining the earth's supply of heat. If we assume that the distribution of radioactive material is uniform throughout the whole globe and the same as is observed near the surface, then we arrive at the result that the rate of evolution of heat by radioactive disintegration would be far greater than the actual rate of loss by radiation into space. In order to explain the steady thermal state of the earth, it is sufficient to assume the existence of a relatively thin surface layer containing radioactive elements in the observed concentration.

We are thus led to the view that the concentration of radioactive elements must decrease rapidly (almost exponentially) with increasing depth. The distance corresponding to a decrease to $1/e$ of the original value is about 13 km. From the chemical properties of uranium and thorium it is plausible that they should be concentrated in the outermost regions as the earth's crust solidified. Taking mean values as a basis, we obtain the following results for the rate of production of heat per $cm.^3$ of rock: from uranium and its products, $4{\cdot}0 \times 10^{-13}$ cal. per second; from thorium, $3{\cdot}7 \times 10^{-13}$ cal. per second; total, $7{\cdot}7 \times 10^{-13}$ cal. per second.

As may be calculated from the mean thermal conductivity of the earth's substance and the temperature gradient towards the centre, the earth radiates 6×10^{12} cal. per second into space. To balance this loss it is necessary, on the basis of the figures given above, to postulate the existence of about $4{\cdot}5 \times 10^{20}$ gm. of thorium and $1{\cdot}2 \times 10^{20}$ gm. of uranium.

If, however, the distribution of thorium and uranium were the same throughout the whole globe as it is at the surface, we should have 12×10^{22} gm. of the former element and $3{\cdot}6 \times 10^{22}$ gm. of the latter. From this we can compute that a surface layer only about 16 km. thick would suffice to maintain the thermal state of the earth, if the distribution were uniform and the concentration equal to that quoted above. Recently a determination has also been made of the rate of evolution of heat in the radioactive disintegration of potassium

It is found that this rate is probably as great as that due to uranium and thorium put together. This naturally affects very considerably some of the numerical results given above.

Determination of the Age of the Earth.—The theory of radioactivity is important in geology because it provides methods for calculating the age of minerals and rocks belonging to different geological periods. It is assumed that during their time of production the minerals in question have been free from disturbing chemical influences. There are three main ways in which the calculation may be carried out. According to the theory of radioactivity a mineral containing uranium must also contain the non-active end-product, radio-lead. The older the mineral, the greater must be the ratio of lead to uranium in it. Moreover, the helium produced in the disintegration is usually retained in the mineral, so that the helium content must be proportional to the age of the mineral. The third method, available in certain special cases, makes use of the small halos, the so-called *pleochroic halos* * (fig. 12), sometimes found in natural crystals. These are a result of bombardment by the α-particles from minute radioactive inclusions over long periods of time. They often show clearly marked rings corresponding to the different ranges of the α-particles from successive members of a disintegration series. These halos can also be imitated artificially.

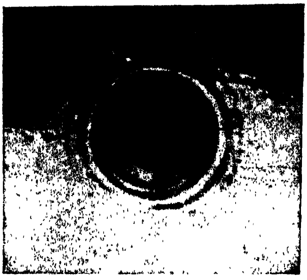

Fig. 12.—Pleochroic halo in a fluorspar crystal (magnification 480)

[From *Zeitschr. f. Physik*, Vol XXVI, 1924 (Springer, Berlin).]

The values obtained by these methods can only be regarded as provisional estimates, but they already constitute an invaluable means for determining the ages of the various geological epochs. The general result is that there actually is a parallelism between the ages deduced on geological grounds and those obtained from radioactive data. The numerical values range from about 8 million years for the Oligocene period, 31 million for the Eocene, 150 million for the Carboniferous (coal), 300 million for the Devonian (first land plants) to about 1000 million for the Precambrian. The first appearance of *life* on the earth was probably about 1200 million years ago. An age of 1600 million years has been found for the oldest gneissoid granites. These values are consistent with estimates based on independent geological considerations.

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* Gr. *pleon*, more, *chrōs*, colour.

C. The Interaction of Matter and Cathode Rays

8. A General Account of the Passage of Electrons through Matter

Historical.—In the year 1892 H. Hertz made the discovery that cathode rays (Vol. III, p. 330) can pass through thin metal foil. A piece of uranium glass, which gives a green fluorescence when exposed to cathode rays, was covered with a very thin sheet of aluminium and mounted in a discharge tube. When cathode rays fell on the metal, the glass underneath fluoresced. Hertz proved that the cathode rays did not pass through holes in the thin metal foil, but actually through the matter (i.e. the metal) itself. Lenard succeeded (1893) in making cathode rays pass out of the discharge tube through a thin aluminium window (see Vol. III, fig. 46, p. 332). This was the first time that the rays had been made available for investigation outside the tube in which they were produced. It now became possible to investigate the interaction between cathode rays and matter independently of disturbing effects due to the discharge tube. Such investigations, extending the work of Lenard, have given us a deeper insight into the nature of electricity and of matter.

The simplest way of detecting the rays passing out through a window is to hold a fluorescent substance in the emerging beam, the most suitable substance being zinc silicate containing manganese. A screen coated with such a substance glows brightly at the spot where the cathode rays strike it. The rays can also be photographed directly, although the eye does not detect them.

We shall now give a general description of the phenomena, reserving a more detailed discussion till later (pp. 39 and 46).

Absorption of Cathode Rays.—Experiments with a fluorescent screen show that the glow is brightest near the window and that it falls off in intensity with the distance. If the tube is working at a potential difference of about 40,000 volts and the aluminium window is a few thousandths of a millimetre thick, the screen remains quite dark when placed at a distance of about 8 cm. from the window. Thus the rays are absorbed to a considerable extent by air at atmospheric pressure. Lenard found that matter behaves in an extremely surprising way with regard to the absorption of these rapidly moving electrons. His result (*Lenard's mass absorption law* 1894), which has been of very great importance for subsequent investigations in atomic physics, may be stated as follows:

To a first approximation the absorption of fast electrons ($v > 0{\cdot}2\ c$, c *being the velocity of light*) *is determined only by the mass of matter traversed and is completely independent of the chemical nature of the substance in question.*

Figs. 13 and 14 are reproductions of two photographic negatives illustrating this property. The plate was covered with strips of different metal foils of the given thicknesses and exposed to the cathode rays in a thin walled plate-holder placed in front of the Lenard window. It is evident (fig. 13) that gold absorbs more strongly than silver (there being less blackening with gold) and that silver absorbs more strongly than aluminium, when all the foils have the same thickness. If, however, the thicknesses are so chosen that the *masses* per unit area are equal (fig. 14), then the absorptions (blackenings) are also equal.

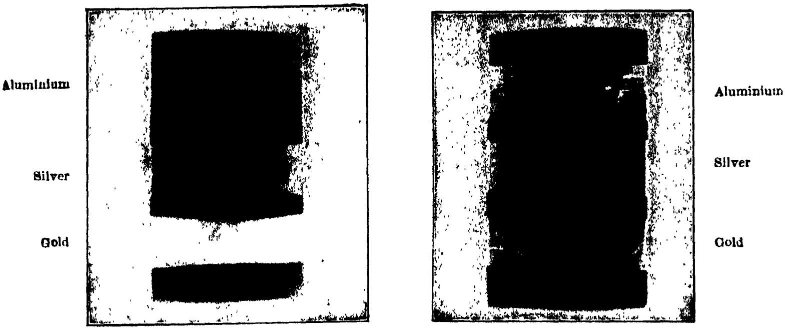

Fig. 13.—Foils of equal thickness (0·00071 mm.)

Fig. 14.—Foils of equal mass (0·75 mg/sq. mm.)

Figs. 13 and 14.—Shadow photographs of various metal foils taken by means of cathode rays in a light-tight, thin-walled plate-holder placed in front of a Lenard window

[From Lenard, *Über Kathodenstrahlen* (Nobel Lecture: J. A. Barth, Leipzig).]

This was the first absolutely inescapable experimental evidence for the conclusion that the atoms of the different chemical elements do not differ qualitatively, but only quantitatively, in their behaviour towards electricity, and must therefore all consist of the same " basic substance " in differing quantities. As we have already explained, this conclusion has been brilliantly confirmed by subsequent investigations. For a further discussion of absorption see p. 42.

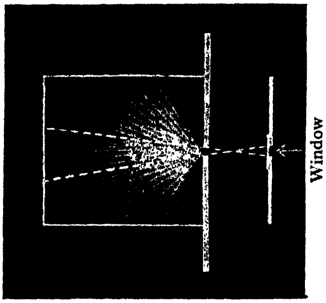

Fig. 15.—Scattering of cathode rays in air

[From Lenard, *Über Kathodenstrahlen* (Nobel Lecture: J. A. Barth, Leipzig).]

Diffusion of Cathode Rays.—Another important phenomenon arises during the passage of electrons through matter. If a wall of absorbing material with a hole in it is placed at a suitable distance from the window of a discharge tube, the appearance shown in fig. 15 is obtained when a fluorescent screen is placed at right angles to the wall (in the plane of the paper in fig. 15). The dotted lines indicate the narrow beam which one would expect to obtain if the rays travelled in straight lines. The cone-shaped spreading of the beam proves that in passing through air cathode rays behave like light passing through a turbid medium. Now the only " turbidity " in the air arises from the molecules in it; hence it must be these that deflect the cathode rays.

Fig. 16 is a diagram (analogous to fig. 15) for hydrogen at a pressure of 40 mm. of mercury. We see that the beam begins to spread noticeably at about 10 cm. from the aperture. The free path for extremely small bodies in hydrogen at this pressure is, however, only 0·002 cm. (Vol. II, p. 50 *). Hence every electron must have passed right through at least 5000 hydrogen molecules without appreciable deviation. The diffusion of cathode rays is due to the *deviation of electrons in their passage through atoms.* Further experiments show that with fast electrons only very small deviations occur in the passage through single atoms, but that as the electron velocity decreases the deflections become greater. Further, if the conditions are otherwise similar the deflection is greater, the greater the atomic weight of the atom. Thus the interior of the atom has an effect upon the electron which we shoot into it as a test body. The only other known causes of deflection of electrons are electric and magnetic fields. Hence the behaviour of electrons gives us information about the fields in the interior of atoms. In this way we actually find that regions of extremely high field strength must exist within atoms, in order that the observed deflections may be produced.

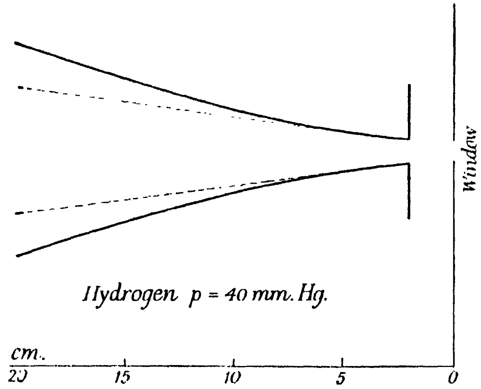

Fig. 16.—Proof that electrons pass through atoms (after Lenard)

Distribution of the Fields of Force in Space.—An insight into the distribution of the atomic fields in space can be obtained from the absorption of cathode rays of different velocities (see further p. 42). As Lenard observed, the fastest electrons with velocities approaching that of light pass through a very large number of molecules without being appreciably affected. The centres of force must therefore be very small. From the number of atoms passed through in the limiting case of very high velocities we can calculate the size of each centre of force (p. 44), that is to say, the fraction of the atomic cross-section which stops all those electrons which fall upon it, no matter how great their velocity. If, for example, we imagine a metre cube of a very heavy substance (say platinum), LENARD's measurements give the result that the total impenetrable volume of all the centres of force contained in the cube is less than that of a pin's head. All the rest of the volume, that is to say, practically the whole of the cube, contains no centres of force, nothing but electric and magnetic fields such as exist in the ether alone. This conclusion of LENARD about the very small size of the centres of force (i.e. the negative and positive charges) forms a foundation for more modern views of the structure of matter.

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* The formula given there must be modified in accordance with Vol. III, p. 307, since we are dealing with particles whose radius is much smaller than that of the hydrogen molecule. The value to be taken for n' is $2{\cdot}7 \times 10^{18} \times 760/40$.

Fig. 17.—Forked electron tracks (secondary electrons of high velocity) (after Bothe)

[From Geiger-Scheel, *Handbuch der Physik*, Vol. XXII, Part II (Springer, Berlin).]

Secondary Rays.—In passing through an atom, an electron of sufficiently high velocity may give rise to such intense disturbance within the atom that one or more other electrons are expelled. These constitute the so-called *secondary cathode rays.* The velocity of the secondary electrons is in general very low, although occasionally very fast secondary electrons are observed. The number of secondary electrons produced, i.e. the probability of their expulsion from an atom through which a fast primary electron passes, is greatest for a certain quite definite velocity of the primary electron. Below a certain primary velocity there are practically no secondary electrons. In cosmic radiation (p. 114) charged particles have been observed of very high penetrating power, far higher than that of any electron, however swift. These particles have been called *mesons.* By measuring the curvature of their tracks in a magnetic field, their mass has been found to be about 180 times the electron mass.

Owing to their low velocities, the secondary electrons are very strongly absorbed by the surrounding molecules. In gases the positively charged atomic residue soon becomes a positive carrier of high molecular weight, while the molecule which absorbs the electron similarly becomes a negative carrier. As was explained in Vol. III, p. 338, this is of fundamental importance for the conduction of electricity in gases.

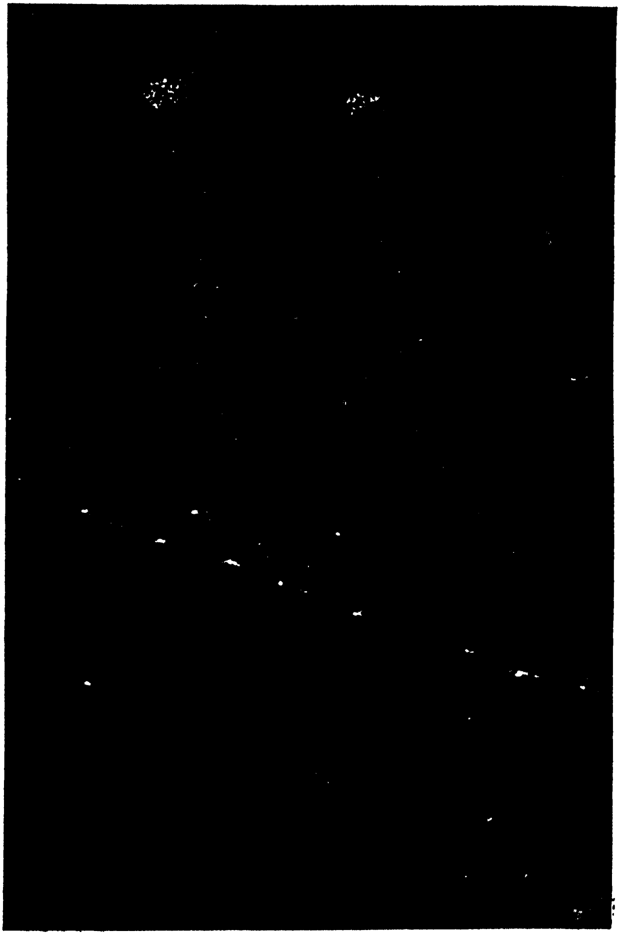

Fig. 18.—Cloud-track photograph of fast electrons showing individual ions

[From *Proc. Roy. Soc.*, A, Vol. CXXXVI.]

Cloud-Track Photographs.—The production of carriers of electricity in the track of an electron makes it possible to render the tracks of individual electrons visible by WILSON'S method (Vol. III, p. 336). What we actually see are the water droplets formed upon the complex molecules of the carriers.

Fig. 17 illustrates the production of secondary electrons of comparatively high velocity—a relatively rare occurrence. The photographs show two forked electron tracks, i.e. two cases in which a relatively large amount of the energy of the primary electron has been transferred to a secondary electron. In the lower photograph about half the energy of the primary electron has been given up to the secondary. These fast secondary electrons can in their turn produce ionization of other atoms or molecules, giving rise to tertiary electrons, and so on. It is to be noted that along the tracks of sufficiently fast electrons the water droplets (which correspond as a rule to single ions) do not occur in pairs only, but also in groups of 4, 6, 8, and more. This corresponds to the production by a secondary electron of 1, 2, 3, or more further electrons. Fig. 18 is a reproduction of a photograph taken by Dee, who succeeded in obtaining such clear tracks that every positive and negative ion is visible as a separate droplet of water. In the case shown in the figure an electric field had been previously applied and was then switched off at the instant of expansion. At this instant a very fast electron passed through the chamber and gave the track visible in the figure. On account of the high velocity of the electron the track is nearly straight. (It can be seen that before the expansion a slower electron also entered through the side.) Under the influence of the electric field the ions have been urged apart, so that two separate rows can be made out, one positive and one negative. The difference between the diffusion of fast and slow electrons is shown very beautifully in fig. 19. The nearly straight track is that of a β-particle and the very crooked ones are those of the much slower electrons liberated by the photoelectric effect from the gas itself. If a magnetic field is applied at the time of photographing, the tracks are made

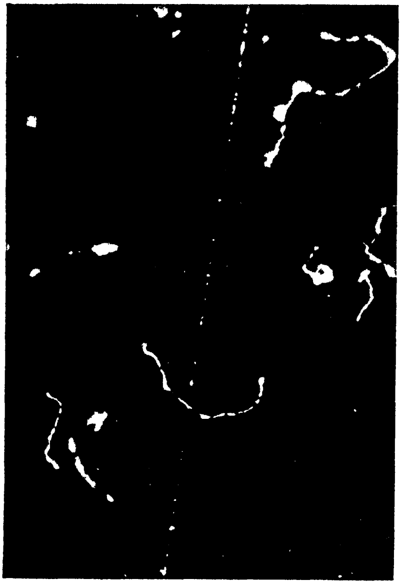

Fig. 19.—Difference between the tracks of very fast and of slower electrons

[From Rutherford, *Radiations from Radioactive Substances* (Cambridge University Press).]

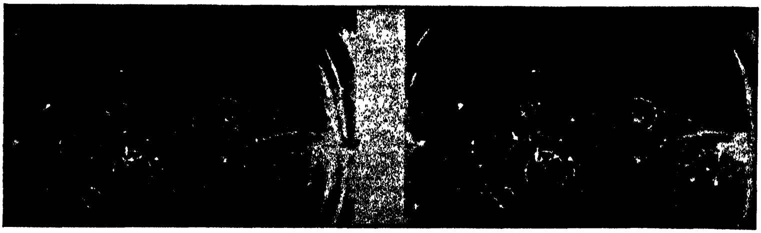

Fig. 20.—Spiral electron tracks in a magnetic field of 1140 gauss (after Skobelzyn, *Zeitschrift für Physik*, Vol. XLIII (1927) (Springer, Berlin))

to curve round the lines of force (see fig. 20) and the velocities of the electrons can be calculated from the observed radii as in Vol. III, p. 324. It is found that in certain cases extremely high energies (up to several hundred thousand volts) are given up by an electron to an atom in passing through it.

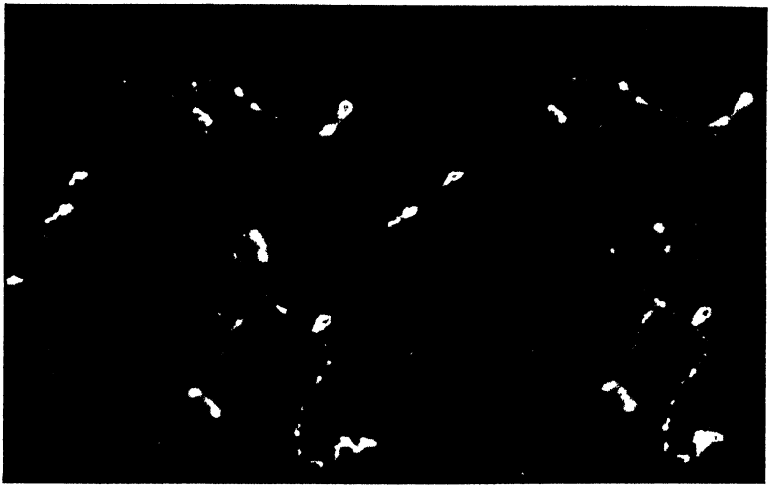

Fig. 21.—Collision of a fast electron with an electron (stereoscopic)

[From Rutherford, *Radiations from Radioactive Substances* (Cambridge University Press).]

Fig. 21 is a photograph showing the direct collision of a comparatively slow β-particle with an electron. The nature of the collision is deduced from the fact that the two tracks are at right angles after the collision. For further cloud-tracks of electrons see figs. 23–26 (pp. 134–136).

Electron Diffraction.—If the atoms of the substance through which the electrons pass are regularly arranged (single crystals, molecules), special phenomena are observed; these will be dealt with later (p. 247).

Excitation of Undulatory Radiations.—If the cathode rays are sufficiently intense, the air near the Lenard window is seen to glow; that is, light is produced in the passage of electrons through matter. It was further mentioned in Vol. III (p. 347) that X-rays are generated by the impact of cathode rays upon matter. For further details see pp. 46 and 137.

9. The Passage of Electrons through Matter: Fundamental Ideas and Quantitative Relationships

Fundamental Ideas.—As cloud-track photographs show, the passage of cathode rays through matter is a very complicated process. Quantitative information is usually obtainable only from the observation of beams containing large numbers of electrons, and it is necessary to understand how the laws of the interaction of electrons and atoms may be derived from the statistical mean values so obtained. The fundamental ideas are for the most part due to LENARD. As a result of the deflections of the individual electrons, an initially parallel beam becomes diffuse as it passes through matter. Eventually a final condition (so-called *complete scattering* *) is reached, in which the diffuseness of the cathode rays has reached the maximum attainable by scattering in matter. In any further passage through the matter in question the directional distribution of the electrons remains unchanged. (Cathode rays emerging completely scattered from a plate have a directional distribution which is the same as that of the intensity of light emitted from an incandescent solid surface (Lambert's law; cf. Vol. IV, p. 24)). It is necessary to distinguish between the *path length* x *of the beam* (i.e. the thickness of the medium measured in the direction of the beam) and the *path length* l *of an electron* (i.e. the total distance actually travelled by an individual electron on its devious course). The latter length is always greater than (or in the limit equal to) the former.

Owing to the many deflections of the individual electron paths in passing through matter, a certain fraction of the electrons are deviated so far away from their original direction as to move backwards relative to the beam. We may refer to this as *large-angle scattering* or *back scattering*.† Thus in the case of a beam of cathode rays incident on thin foil, some electrons pass through and out at the other side, and some return and pass out at the original side owing to back scattering. The relative number of backward-scattered electrons at first increases with increasing thickness of the layer of matter, gradually approaching a limiting value (for the thickness x_R, say). The fraction of the incident electrons returned by an infinitely thick plate may be called the *back scattering constant* p. The ratio of the electron path length l to the beam path length x in the final steady state (complete scattering) gives a measure of the extent to which the electron paths are deviated. This ratio B enables us to calculate true electron path lengths from beam path lengths and to draw conclusions which are independent of the devious paths followed by individual electrons.

Table V gives numerical values for two velocities. Here, as in future, the electron velocities are expressed in terms of the ratio β of the actual velocity v to that of light c, i.e. $\beta = v/c$.

Diminution of Velocity.—The true rate of decrease of velocity with distance measured along the *electron path* (i.e. dv/dl) cannot be measured directly. What is obtained in actual measurements is the rate of decrease of velocity with distance measured along the beam (i.e. dv/dx) for the majority of the electrons in the final state and for equal angles of entry and exit. Greater and smaller velocity changes also occur, but only in the case of a minority of the electrons.

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* Ger. *Normallauf.*

† Ger. *Rückdiffusion.*

TABLE V

Scattering Medium	$\beta = 0{\cdot}35$			$\beta = 0{\cdot}92$		
	p	B	x_R cm.	p	B	x_R cm.
Vacuum . .	0	1	—	0	1	—
Aluminium . .	0·28	1·8	0·00014	0·23	1·6	0·07
Silver	0·60	4·0	--	(0·46)	(2·7)	—
Gold	0·68	5·3	0·00008	(0·56)	(3·6)	—

Fig. 22 shows the velocity losses in aluminium graphically. The losses plotted as ordinates refer to a thickness of 0·01 mm. For other substances the values of dv/dx have a more rapid increase than that corresponding to proportionality to mass. The true rate of decrease in velocity with distance measured along the electron path (i.e. dv/dl) is approximately proportional to mass. Thus in a material with a density twice that of aluminium the corresponding values of dv/dl are approximately twice as great, while the values of dv/dx are more than twice as great. This is due to the fact that with the denser elements, most of which possess higher atomic weights, the deviations of the electron paths are greater.

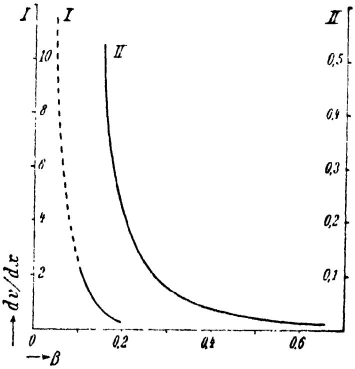

Fig. 22.—Velocity loss of electrons (completely scattered) in the direction of the beam (0·01 mm. aluminium) (after Becker).

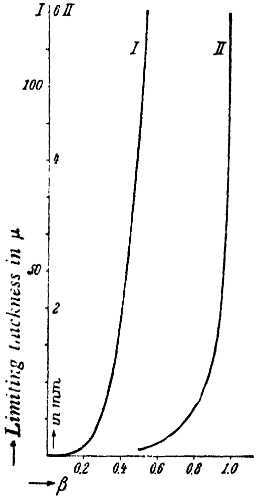

Fig. 23.—Limiting thicknesses in aluminium for different electron velocities (after Lenard).

Limiting Thickness and Range.—For every substance there exists a more or less well-defined thickness (*limiting thickness x*) which will reduce to zero the velocity of a beam of cathode rays in the state of complete scattering. (The velocity referred to here is that mentioned above, viz. that of the majority of the electrons in the beam.) Fig. 23

gives the relationship between limiting thickness and electron velocity for aluminium. Of still greater interest are the actual lengths of path (l_0) traversed by the electrons before they are completely stopped (true ranges). These can be calculated approximately by multiplying the limiting thickness by the factor B referred to above. Direct cloud-track photographs show that for a given initial electron velocity the maximum electron range l_0 in any given medium is more or less the same for all the electrons (see figs. 23, 26, pp. 134, 136).

Absorption.—The most marked effect in the passage of a homogeneous beam of cathode rays through a plate is not the diminution of velocity dealt with above, but a diminution in the actual number of electrons. This latter effect depends upon the initial velocity, the nature of the material of the plate, and the directional distribution at incidence. For thicknesses greater than x_R (see above, p. 40), however, it becomes independent of the distribution at incidence, and in this case the number n_0 of electrons for a thickness X (greater than x_R) is connected with the corresponding number n for the thickness (X + x) by means of the equation

$$n = n_0 e^{-ax}.$$

The constant a, which has the dimensions of the reciprocal of a length, is called the *practical absorption coefficient,* while the quotient of a and the density ρ of the absorbing material is called the *practical mass-absorption coefficient.*

Variation of Practical Absorption Coefficients with the Nature of the Material.—It has already been mentioned (p. 33) that the absorption of fast electrons is proportional to the absorbing mass. Table VI gives values for various materials.

TABLE VI

Substance	a	ρ	a/ρ
Hydrogen (760 mm.)	0·467	0·0000849	5610
Air (760 mm.)	3·42	0·00123	2780
Aluminium	7150	2·7	2650
Copper	23800	8·9	2670
Silver	32200	10·5	3070
Gold	55600	19·3	2880

For velocities lower than $\beta = 0{\cdot}1$ the absorption is no longer proportional to mass. Here the gas-kinetic * molecular cross-section or free path of the electrons becomes effective, and different substances accordingly behave differently. At moderate velocities H_2 behaves abnormally (see Table VI) in showing an absorption 1·8 times greater than that expected, while He shows an absorption 0·7 times greater than that corresponding to proportionality to mass. All hydrogen compounds likewise show anomalously high values, and the same is true of Cl, Br, and I.

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* Following Andrade (*Structure of the Atom,* 3rd Ed., p. 10 (G. Bell & Sons, 1927)), we use this conveniently short word to translate the German *gaskinetisch.*

Variation of Absorption with Velocity.—The smaller the electron velocity, the greater is the absorption. This is evident from the values given in Table VII, which show that matter becomes more and more penetrable as the velocity of the electrons is increased. Thus the average number of atoms passed through in air and aluminium before an electron is absorbed is 18,000 for a velocity giving $\beta = 0{\cdot}35$ and 4,500,000 for $\beta = 0{\cdot}92$. It is very remarkable that in the case of a stream of electrons of uniform velocity incident upon an absorbing layer, the electrons passing through do not exhibit a range of velocities from zero to an upper limit, but have one more or less well-defined velocity (p. 40), which is lower than the original incident velocity. Again, the diminution of velocity is very much less marked than the actual diminution in the number of electrons (or intensity of the beam). When the velocity of the emergent electrons is reduced to half, the number is reduced to quite a different order of magnitude. For $\beta = 0{\cdot}3$ only 1·5 per cent of the passages through atoms cause appreciable velocity reduction; for $\beta = 0{\cdot}9$ only 0·085 per cent. Since the direction of motion also remains practically unaltered in the majority of cases, it follows that *in such cases the electron flies right through the atom without being subject to any appreciable forces.*

TABLE VII

β	a/ρ	β	a/ρ	β	a/ρ
0·9	6	0·4	$7{\cdot}4 \times 10^2$	0·06	$2{\cdot}5 \times 10^6$
0·8	$1{\cdot}3 \times 10$	0·3	$2{\cdot}9 \times 10^3$	0·04	$5{\cdot}8 \times 10^6$
0·7	$2{\cdot}9 \times 10$	0·2	$3{\cdot}6 \times 10^4$	0·02	$1{\cdot}3 \times 10^7$
0·6	$8{\cdot}3 \times 10$	0·1	$8{\cdot}0 \times 10^5$	0·01	$1{\cdot}8 \times 10^7$
0·5	$2{\cdot}2 \times 10^2$	0·08	$1{\cdot}4 \times 10^6$	(0·00)	$2{\cdot}0 \times 10^7$

Thus the greater the velocity of an electron, the smaller is the probability that it will interact with an atom through which it passes. This behaviour can be seen very clearly in the cloud-track photographs of figs. 18, 19 (pp. 37, 38).

Absorbing Cross-section. — The greater penetrability of atoms at high electron velocities may be expressed by ascribing to each atom an absorbing cross-section Q which decreases as the electron velocity increases. The absorption coefficient may then be regarded as the total area of the absorbing cross-sections of all the atoms in one cubic centimetre. This is in agreement with the dimensions of the absorption coefficient (see above), namely $[\text{cm.}^{-1}] = [\text{cm.}^2/\text{cm.}^3]$.

The absorbing cross-section of a molecule or atom is obtained by dividing a by Avogadro's number (Vol. II, p. 52).

At low electron velocities (not below 10 volts) the absorbing cross-section for air is found to be about 30 per cent greater than the gas-kinetic cross-section. This means that electric fields exist outside the volume regarded as impenetrable in the collision of molecules according to the kinetic theory. For greater electron velocities the absorbing cross-section falls off for all substances. Particular interest attaches to the value corresponding to $\beta = 1$, i.e. to electrons with the speed of light, for this must represent the cross-section of that part of the atom which is completely impenetrable to electrons. For $\beta = 0 \cdot 99$ the value for air is only $2 \cdot 4 \times 10^{-8}$ of the ordinary gas-kinetic cross-section. This means that the radius of the impenetrable area (supposed circular) corresponding to a pair of elementary charges (electron and proton—LENARD's "dynamid") has a limiting value of about 3×10^{-12} cm. Thus we arrive at the following extremely important result (obtained quantitatively by LENARD as early as 1903): *the effective radius of the electron and also of the proton must be less than* 3×10^{-12} *cm.* (See further p. 82.)

Since the true absorbing cross-section per unit mass falls off in general as the atomic weight increases, we are led to the conclusion that in the elements of higher atomic weight the charges must be more densely concentrated. The decrease of a/ρ as we pass from H to He is especially marked, and indicates that in He the positive charges must be very closely packed—a conclusion that makes it easy to understand the extreme stability of α-particles.

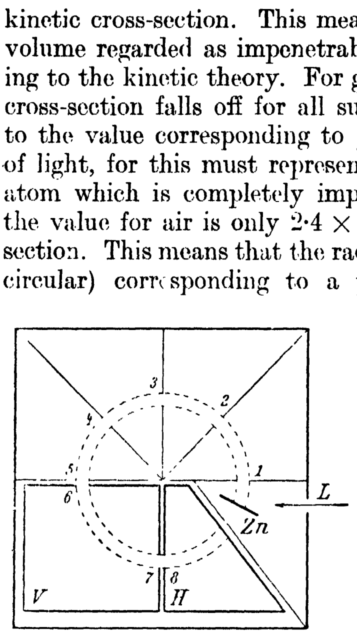

Fig. 24.—Ramsauer's circle method

Effective Cross-section for Very Slow Electrons (the Ramsauer Effect).—A quite unexpected phenomenon was discovered by RAMSAUER in the course of his experiments on the passage of very slow electrons through gases (1921). He found that argon is *almost completely permeable* to electrons with velocities of about 0·4 volt and that at these velocities there is no scattering.

At this point a short account may be given of RAMSAUER's method (the so-called *circle method*), which is of considerable importance for the investigation of electrons. A small metal box (fig. 24) contains a zinc plate Zn, from which the electrons are liberated photoelectrically. The whole apparatus is placed in a magnetic field (the lines of force being perpendicular to the plane of the figure), so that the electrons move in circular paths. The apertures 1, 2, 3, 4, 5 in screens serve to select electrons of definite velocities. The cages V and H are insulated from the main framework of the apparatus. If V and H are connected

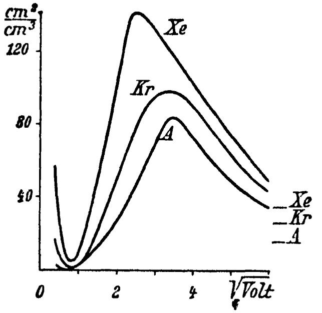

Fig. 25

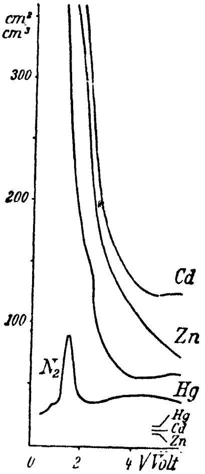

Fig. 26

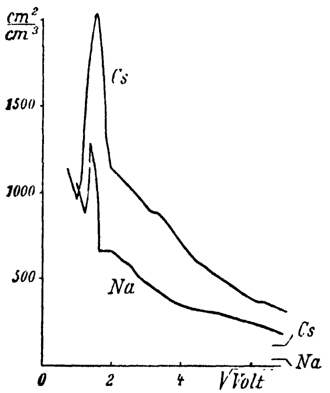

Fig. 27

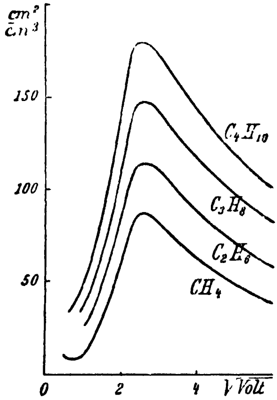

Fig. 28

Figs. 25, 26, 27, and 28.—Effective cross-sections for different gases reduced to 0° C. and 1 mm. Hg.

to each other and to an electrometer, a measure is obtained of the total number of electrons passing through the aperture 6. If only H is connected to the electrometer, a measure is obtained of the fraction of the electrons that passes through V without appreciable diminution of velocity and without absorption or alteration of direction. Those electrons whose velocity is diminished have their paths more strongly bent in the magnetic field and so fail to enter H. Different velocities can be investigated by altering the strength of the magnetic field, and different gases and gas pressures can be used.

What is measured in the above method is the so-called *effective cross-section* of the atoms or molecules of the gas, i.e. that cross-section which is effective in influencing the electrons, either by stopping them or by altering their velocities or directions of motion. Figs. 25, 26, 27, and 28 show examples of the results obtained. The gas-kinetic cross-sections are plotted as ordinates to the right of the figures. The effective cross-section of the atoms of the inert gases increases at first as the electron velocity decreases down to about 10 volts, when it is much greater than the gas-kinetic value. Thereafter it falls off again almost to zero for slower electrons, but probably rises again finally for velocities below $\frac{2}{3}$ to $\frac{1}{3}$ volt. The paraffins also show a similar marked falling-off of the effective cross-section for slow electrons. In contrast to this the values for Hg, Zn, Cd, and in particular the alkali metals (the ordinate scale in fig. 27 is much smaller than in the other figures), show a very remarkable increase with decreasing electron velocity.

As was mentioned above, there are three processes to be taken into account in giving an explanation of effective cross-sections: (1) deflections without loss of velocity (elastic collisions); (2) partial loss of velocity (inelastic collisions); and (3) complete loss of velocity (absorption).

The parts played by these three processes are not yet known with certainty. The maximum of the curves, however, does not seem to depend on the onset of absorption, but on deflections without energy loss.

10. Energy Transformations in the Passage of Electrons through Matter

Secondary Electrons.—The total number of secondary electrons produced in the passage of a primary beam of electrons through the atoms and molecules in 1 cm. of path (i.e. in a layer of the medium 1 cm. thick) is called the *differential* secondary effect. If the primary velocities are large, many of the secondary electrons may themselves liberate further electrons in passing through atoms (so-called tertiary electrons, and so on); it is therefore necessary to distinguish between the total differential secondary effect and the *pure* differential secondary effect, i.e. the number of electrons produced per 1 cm. layer by the *primary* electrons alone. We may use S_t to denote the total number of electrons (or pairs of carriers) produced along the *whole length of an electron track*. Table VIII gives some numerical data on secondary electrons for various primary velocities; s is the total differential secondary effect, s' the pure differential secondary effect, in air under normal conditions.*

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* The values in brackets are uncertain.

TABLE VIII

β	$s - s'_{\text{cm.}^{-1}}$	S_l	β	$s_{\text{cm.}^{-1}}$	$s'_{\text{cm.}^{-1}}$	S_l
0	0	0	0·4	250	250	1440
0·006	0	0	0·5	180	180	2450
0·024	7700	($\sim$5)	0·6	131	131	(4000)
0·05	3200	20	0·7	95	89	(6300)
0·1	1700	80	0·8	69	53	(10500)
0·2	830	320	0·9	50	25	(20000)
0·3	400	760	0·99	41	2	($\sim$100000)

The mean energy loss of a primary electron in passing through and ionizing an atom appears to be about 30 to 40 electron volts. This value appears to hold approximately for all elements (for air it is about 32·2 electron volts), with the exception of the halogens, for which the loss is considerably smaller. As is shown by cloud-track photographs, the loss of energy of a moving electron as a rule takes place in a very large number of small steps, each of the above magnitude. Hence we have $S_l = U/\epsilon$, where U is the initial energy and $\epsilon = 32·2$ volts for air. The average velocity of the secondary electrons, however, is much smaller. The nature of the energy distribution in this case is still obscure. With very high primary velocities a considerable number of fast secondary electrons are also produced with velocities up to several thousand volts (fig. 17, p. 36). This can be seen from the differences between the corresponding values of s and s' (p. 46) in Table VIII. The number of secondary electrons is to a first approximation proportional to the mass and independent of the state of aggregation. Hydrogen forms an exception, as it gives many more secondary electrons than the number corresponding to proportionality to the mass (up to twelve times as many). This is true for hydrogen compounds as well as for the element itself.

The production of secondary electrons in insulating media is associated with the appearance of electrical conductivity, and this may be used to measure the intensity of cathode rays. As is shown by Table VIII, no secondary effect is produced below a certain limiting velocity of about 11 volts ($\beta = 0·006$). The differential secondary effect thereafter increases rapidly to a maximum at the optimum velocity, which lies in the neighbourhood of 130 to 150 volts ($\beta = 0·024$) for most substances. At higher velocities s then gradually falls off again.

Secondary electrons are also emitted from the surface of a solid upon which a primary beam is incident. Under suitable conditions the solid body may become positively charged, since the number of secondary electrons lost may exceed the number of primary electrons captured.

Not every passage of an electron through an atom gives a secondary electron; this is especially true at high velocities. Apparently it is only at the optimum velocity that every such passage causes ionization. The resulting ion and secondary electron then very quickly form carriers of greater molecular complexity.

Energy Relationships in the Collisions of Very Slow Electrons with Atoms.—A general account will first be given of the method for measuring the velocity distribution of electrons in a beam, first used by LENARD and subsequently applied in very widely varying ways.

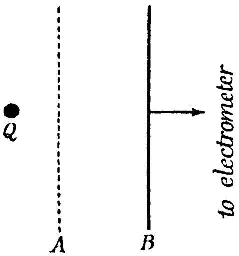

Fig. 29.—Lenard's retarding field method

The electrons, whose velocity distribution in the space between A and B (fig. 29) is to be determined, are emitted from the source Q, pass through a grid placed at A, and fall upon a plate (or box) at B. A potential difference, which can be varied at will, is now applied between A and B, so that B is negative relative to A. The electrons entering the space between A and B thus pass into a retarding field. Suppose that the potential difference between Q and A is U_0; then the kinetic energy of the entering electrons is eU_0. The work done in passing through the opposing potential difference U between A and B is eU, and hence the energy on arrival at B is $e(U_0 - U)$, i.e. the volt-velocity at B is $(U_0 - U)$.

If $U = U_0$, the velocity of the electrons is just reduced to zero at B, and they are then driven back again to A by the field. In the case of a beam containing electrons of different velocities, the retarding potential U will prevent those electrons with volt-velocities smaller than U from getting to B. The current between A and B can be measured. It is given by the number of electrons passing between A and B in unit time, and hence falls off as the retarding potential is increased, by an amount corresponding to the number of electrons of velocity less than U. Fig. 30 shows one of these current-potential curves. In this case the highest velocity in the electron beam is 20 volts, so that the current becomes zero for a retarding potential of this magnitude. For this value and higher values of the retarding potentials all the electrons passing through A will be turned back by the field before reaching B, those of low velocity after a short distance and those of higher velocity after a correspondingly greater distance. This turning back of the electrons is analogous to the falling back to earth of stones thrown upwards against the earth's opposing gravitational field. The slope of the curve at any given potential (i.e. dI/dV at this point) is a measure of the number of electrons which just fail to reach B at this potential, i.e. the negative fraction of the electrons possessing the corresponding velocity (or, more exactly, possessing velocities lying in the range dV). Thus in fig. 30 the current decreases from 90 per cent to 60 per cent as the potential is changed from -5 volts to -15 volts. This indicates that 30 per cent of the electrons have velocities lying between 5 and 15 volts. Hence the derived curve of the current-potential curve is the velocity distribution curve. Fig. 31 is obtained in this way from fig. 30. (*Method of the retarding electric field.*)

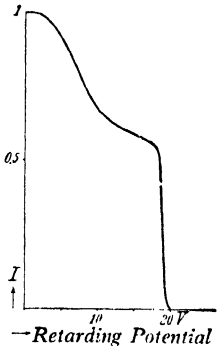

Fig. 30.—Current-potential curve for the retarding field method.

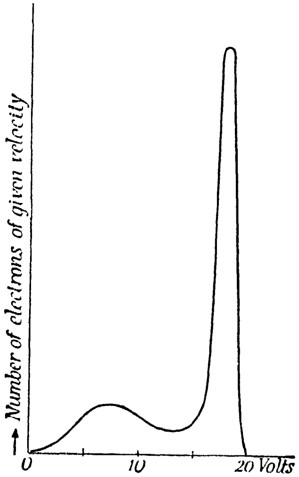

Fig. 31.—Velocity distribution curve corresponding to fig. 30

Ionization Potentials. Resonance Potentials.—As has already been stated on p. 36, electrons of very low velocity are not able to produce secondary electrons by interaction with atoms or molecules. Lenard showed (1902) that a certain minimum primary velocity is necessary before secondary electrons (and the residual positive ions) are produced. He used a method identical in principle with that outlined above. The electrons, accelerated to a definite velocity, entered a box in which they collided with gas molecules. Within the box was a ring R (fig. 32) which was maintained at a sufficiently high negative potential and connected with an electrometer. The primary electrons were unable to reach this ring on account of the opposing field; but the positive carriers or ions produced were attracted to it. Ionization consequently gave a positive charge on the electrometer. With this

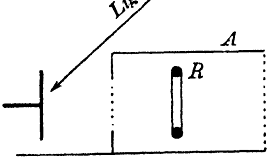

Fig. 32.—Lenard's apparatus for the measurement of ionization potentials.

apparatus it was found that, under the experimental conditions, a minimum primary electron velocity of about 10 volts was required (see fig. 33) before positive ions were produced, i.e. before secondary electrons were liberated. The potential required to remove an electron from an atom is called the *ionization potential.* The value found by Lenard is that appropriate to the mercury atoms which are always present in evacuated tubes (coming from the pumps) unless they are removed by condensation in a trap cooled with liquid air. Later experiments have shown that quite definite ionization potentials are associated with each kind of atom. The lowest ionization potential is that of Cs (3·9 volts); the highest that of He (24·5 volts). A table of ionization potentials for the various elements, some of which are obtained by other methods, is given on p. 301. In extending the work of Lenard with an apparatus similar in principle to that of fig. 32

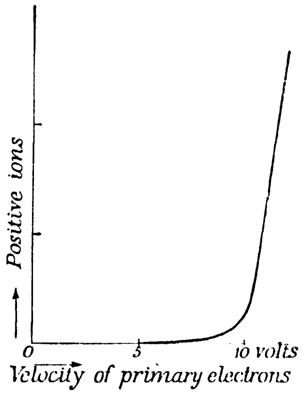

Fig. 33.—Determination of ionization potential (Lenard, 1902)

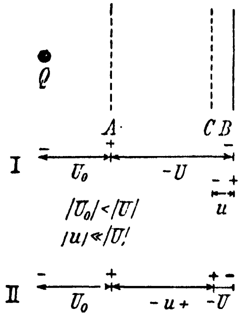

Fig. 34.—I. Diagram of apparatus for measuring resonance and ionization potentials separately.
II. Arrangement for more accurate measurement of resonance potentials.

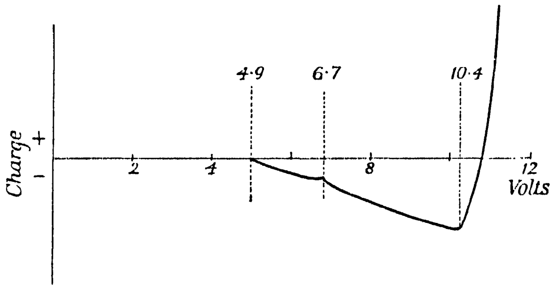

Fig. 35.—Resonance potentials and ionization potential of mercury (after Davis and Goucher)

(p. 49), but using an electrode with a large surface area instead of the ring, **Franck** and **Hertz** (1913) found that positive charges were produced ever at much lower definite potentials. They concluded that this was due to the existence of correspondingly low ionization potentials. Actually, however, **van der Bijl** (1916) was able to show that the positive charges were really due to a photoelectric effect at the large surface of the electrode, an effect which **Lenard** had avoided by the choice of a thin ring. It follows that in the experiments of **Franck** and **Hertz** light must have been produced in the gas at the potentials which they observed. This was quite a new phenomenon, and one that clearly involved the transfer of energy to atoms from electrons at definite potentials, the energy being transformed into light. The potentials at which such transfers just begin (i.e. definite energy losses of the electrons without production of secondary electrons) are called *resonance* or *radiation potentials*.* In order to distinguish between ionization and resonance potential effects, it is necessary to modify **Lenard**'s apparatus slightly. This modification, which is due to **Davis** and **Goucher** (1917), is represented in fig. 34. In front of the electrode B, which is maintained at the negative retarding potential, is placed a grid C. This is kept at a small negative potential relative to B. Then if light emitted in the gas liberates photo-electrons from B, the field between B and C will drive them back again. Indeed, B will become negatively charged by the electrons liberated photo-electrically from C. Not until positive ions are produced in the gas will B become positively charged, owing to their being attracted through the grid. Fig. 35 shows the results of experiments with mercury vapour. Resonance potentials are seen to occur at 4·9 and 6·7 volts, while the production of positive ions at 10·4 volts indicates an ionization potential at this point.

With an apparatus embodying the same principle very accurate measurements of resonance potentials can be made, once the ionization potential has been determined with sufficient certainty. It is merely necessary to use a different potential distribution, as shown in fig. 34 II. Here there is only a small potential difference between A and C, so that the electrons making collisions in this region all have very nearly the same velocity. The quantity measured includes both the positive charge due to photo-electric liberation of electrons from the electrode and also the effect of the energy losses of the primary electrons. Fig. 36 shows the results of experiments, again with mercury, from which a large number of resonance potentials can be detected. (Those resonance potentials whose existence would be uncertain, judging by this curve alone, are confirmed by other observations.) The existence of sharply defined energy steps in the transference of energy to atoms is extremely important in connexion with the more detailed theory of light emission.

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* Ionization and resonance potentials are often included together in the term *critical* or *excitation potentials*.

Elastic Collisions at Low Velocities.—Franck and Hertz also investigated the energy exchanges at still lower velocities. Their experiments upon electrons scattered back from a region containing an inert gas showed that most of these back-scattered electrons have a velocity equal to that of the incident electrons. From this we conclude that back scattering in inert gases (as also in other gases, e.g. metal vapours) must consist of a large number of elastic collisions without appreciable loss of velocity (or energy). For the velocity loss on elastic collision see p. 89; the thermal motions of the molecules, which correspond to an electron-volt-velocity of a few hundredths of a volt, may be neglected. More detailed calculations based on the experimental data show that in helium electrons of very low velocity

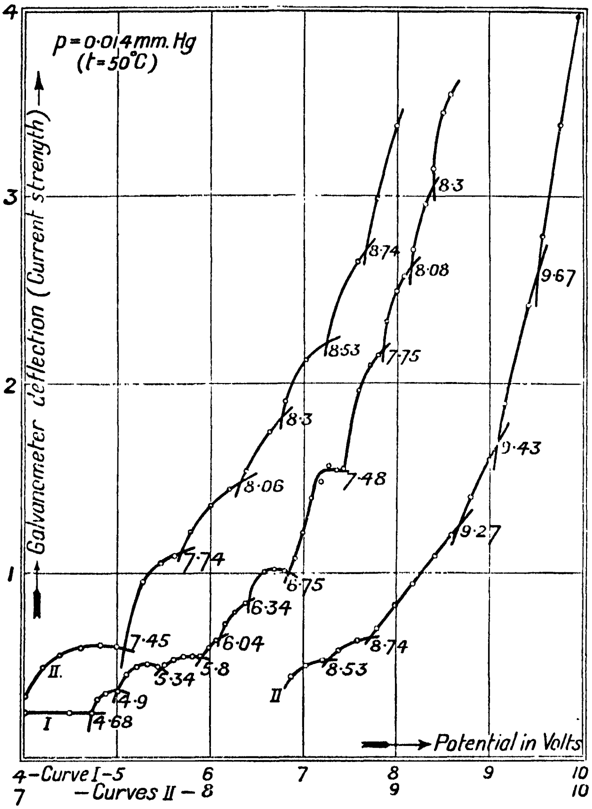

Fig. 36.—Resonance potentials of mercury (Franck and Einsporn)

may participate in many thousand encounters without a greater loss of velocity than that corresponding to elastic collisions.

In other gases whose atoms or molecules readily pick up electrons (i.e. gases with so-called electron affinity) considerable velocity losses are observed. Their more exact explanation is not yet possible.

Energy Transformations. — From about $\beta = 0{\cdot}3$ upwards the energy given up in the velocity losses of electrons passing through matter is transformed almost entirely into secondary rays. In addition to secondary electrons, electromagnetic radiations are produced, i.e. " light " of the most widely differing wave-lengths. We have to distinguish between two different processes. In the first place, the primary electron itself gives rise to an electromagnetic radiation on account of its retardation. So far this has only been proved for the higher electron velocities (>1000 volts), in which case the radiation lies in the X-ray region. In consequence of the retardation of the electron an electromagnetic disturbance is set up, which is propagated with the velocity of light. According to the principles given in Vol. III, the electric field strength of the disturbance is proportional to the retardation of the electron, while its direction is that of the projection of the direction of motion of the electron upon a plane perpendicular to the direction of propagation of the light. The wave-lengths of these radiations can be determined experimentally by the usual methods. The way in which these radiations are produced leads us to expect a spectrum containing a whole range of wave-lengths (i.e. a continuous spectrum). In actual fact, experiments have shown that the spectrum comes to an end at a certain definite short-wave limit (DOUANE and HUNT, 1915). As will be explained on p. 59, the position of this limit bears a simple relationship to the primary electron velocity. The radiation here referred to is generally called the *continuous X-ray spectrum* or (by analogy with white light) " *white* " *X-radiation.**

In addition to the " white " radiation, electromagnetic waves are emitted which are *characteristic* of the particular atom with which the electrons collide. These radiations originate in energy changes within the atom, caused by the electron impact (p. 73). Their wave-length depends upon the energy of the electron. For slow electrons they lie in the visible region; for fast electrons, in the X-ray region. The particular wave-length depends upon the nature of the atom concerned. There is another way, however, in which the atom may lose the energy taken up from the electron: this energy may be transformed directly into thermal energy by gas-kinetic encounters (so-called *collisions of the second kind*, p. 160).

The amount of cathode ray energy E_W transformed into " white " radiation is given approximately at the higher velocities (measured from 0·05 to 0·5 of the velocity of light) by the formula $E_W = ZeU \times 10^{-9}$, where Z is the atomic number (p. 5) of the target and U the volt-velocity of the electrons.

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* Ger. *Bremsstrahlung*, literally, deceleration radiation.

The behaviour of atoms as regards the emission of characteristic radiation will be dealt with later (visible region, p. 186; X-ray region, p. 291).

D. The Interaction of Matter and Short-wave Electromagnetic Radiation

11. Absorption and Scattering of X-rays

As has already been stated in Vol. III and on p. 53 above, the incidence of rapidly moving electrons upon matter gives rise to X-rays. These are electromagnetic waves (Vol. III, pp. 347 and 646; Vol. IV, pp. 12, 165) of wave-length from 100 to 0·01 Å, detectable by their effect upon a photographic plate, by the fluorescence which they produce in certain materials, e.g. barium platinocyanide, and by the electrical conductivity which they induce in gases.

As X-rays pass through matter (e.g. through air or metal foil) there is a diminution of intensity which can be demonstrated photographically or by the reduced ionization. This diminution of intensity varies very much for X-rays of different wave-length, the shorter waves being as a rule much less affected than the longer waves. Hence the effect provides a practical method for roughly determining the wave-length region.

The diminution of intensity is accompanied by two main effects. As has already been mentioned, air through which X-rays pass becomes *conducting*. In addition, X-rays can be detected beyond the limits of the direct beam, which may be defined by lead screens or the like (the so-called **secondary radiation**). These secondary X-rays are particularly strong when a comparatively dense substance is placed in the path of the primary rays.

Formation of Carriers or Ions.—When a beam of X-rays passes through a cloud-chamber, tracks of the kind shown in Vol. III, fig. 54, p. 337 are obtained. The tracks, which proceed from individual atoms in the path of the beam, prove, by their curvature in a magnetic field and by the number of ions in comparison with their length, to be electron tracks. Thus the X-rays eject electrons from the atoms upon which they fall, sometimes (as measurements of the range show) with considerable velocity. Here we are dealing with a photo-electric effect (p. 133), a phenomenon which becomes especially marked in this short-wave region.

The emission of these **photo-electrons** is found to be independent of the direction and state of polarization of the X-rays. Hence we must conclude that energy from the beam is taken up by the atom and there transformed into some kind of atomic energy which finally leads to the emission of an electron. The details of this process will be discussed on p. 117. The observed conductivity of the air in the path of X-rays is to be regarded as due to the removal of electrons in the photo-electric effect.

Provided that care is taken to ensure well-defined conditions, the conductivity produced by a beam of X-rays may be used as a measure of intensity. The actual method is to allow the rays to enter a suitable cylindrical condenser (a so-called *ionization chamber*) along the axis. Between the electrodes of the chamber is applied a potential high enough to produce the saturation current, the strength of which is then measured with a galvanometer or an electrometer.

The shorter the wave-length of the X-rays, the more marked becomes another mode of ejection of electrons from atoms upon which the rays fall. The electrons ejected in this effect, which is *not* independent of the direction and state of polarization of the rays, are generally referred to as **recoil e'ectrons**. A more detailed treatment of the phenomenon is given on p. 235.

Fig. 37 shows a cloud-track photograph of X-rays of very short wave-length passing through hydrogen, in which this effect is exhibited particularly well. In addition to the very irregularly distributed photo-electrons, which travel far beyond the path of the X-ray beam (actual width 0·6 mm.), a number of short electron tracks can be seen, nearly all running in the direction of the beam. These are tracks of recoil electrons, which are thus seen to be ejected predominantly in the direction of the X-rays.

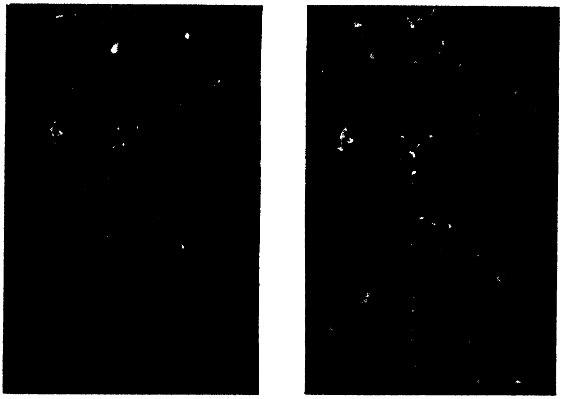

Fig. 37.—Cloud-tracks of the photo-electrons and recoil electrons (the latter showing as short tracks in the direction of the beam) produced by a beam of short-wave X-rays in hydrogen (after Bothe). (Stereoscopic.)

Secondary X-rays.—A substance (e.g. a piece of metal) placed in the path of a beam of X-rays itself becomes the source of X-rays, which are propagated in all directions and may be detected by means of a photographic plate or an ionization chamber shielded from the primary rays by a thick sheet of lead.

Absorption measurements or spectroscopic investigations (Vol. IV, p. 209) show that the secondary X-rays consist of two distinct constituents. The first is identical with the primary rays and is due to the scattering of these by the atoms of the substance, just as light is scattered in milk. This component is therefore referred to as **scattered radiation.** In the second place, we obtain X-rays which vary with the individual character of the substance in question—so-called **characteristic radiation.** The production of this latter type of radiation is analogous to the fluorescence observed with ordinary light, i.e. the phenomenon in which a substance (e.g. uranium glass or a solution of the sodium salt of fluorescein) emits a characteristic light of definite spectral composition when illuminated with light of sufficiently short wave-length. The fluorescent light is nearly always of longer wave-length than the exciting light. So also for the characteristic X-radiation: its wave-length is longer than the shortest wave-length occurring in the primary X-rays. Hence it is sometimes referred to as **fluorescence radiation.** Its wave-length decreases regularly as the atomic number of the element increases (p. 75). It is characterized by great homogeneity, i.e. it consists of practically monochromatic X-rays or of a mixture of a few sharply defined wave-lengths. Fig. 46, Plate XVI, Vol. IV (p. 210) gives an idea of the sharpness of the spectrum lines of these characteristic X-rays (in this case the fluorescence radiation from aluminium). BARKLA, and later SIEGBAHN, succeeded in proving the existence of several sharply defined groups of characteristic wave-lengths for each element. The group of shortest wave-length is called the K-radiation, the groups of longer wave-length the L-, M-, N-radiation, and so on. For further details see p. 73.

Polarization of X-rays.—The passage of X-rays through matter is analogous to the passage of ordinary light through a turbid (and at the same time fluorescent) medium (the TYNDALL effect, Vol. IV, p. 232). In the case of X-rays the turbidity arises from the atoms and molecules, whose dimensions (10^{-7} to 10^{-8} cm.) are no longer small relative to the wave-length. Just as in the case of ordinary light, the scattered rays are polarized (p. 57). The proof of the existence of this polarization by BARKLA was of historic importance in connexion with the recognition of the transverse undulatory nature of X-rays.

We shall begin by considering the optical experiment which is analogous to that of BARKLA. From a source L (fig. 38) the light passes through a layer of a turbid medium K (e.g. a trough containing an emulsion of mastic). The scattered light is polarized in the plane determined by the primary beam and the direction of observation. Thus the layer K acts as a polarizer. A second layer K′, which is screened from the primary light, is irradiated by the light which has been scattered and polarized in this way. The light scattered from this second layer shows a maximum of intensity in the direction Z parallel to the original direction LK. At right angles to this (i.e. in the figure at right angles to the plane of the paper) the intensity of the scattered light is a minimum. Thus the layer K′ acts as an analyser (cf. Vol. IV, p. 232). The same experiment may be made with X-rays, in which case L is replaced by an X-ray tube, K and K′ by blocks of carbon or paraffin wax, and the eye by an ionization chamber (see fig. 39). Carbon is chosen because the characteristic radiation of this element is absorbed by the air, leaving only the scattered radiation to affect the chamber. The chamber is placed at J_1 or in a position at right angles to this either above or below the block K′. As in the case of ordinary light, a maximum is found at J_1 and a minimum in the other position.

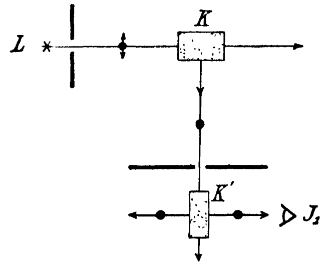

Fig. 38.—Determination of the polarization of light scattered from a turbid medium. ● = electric vector normal to plane of figure.

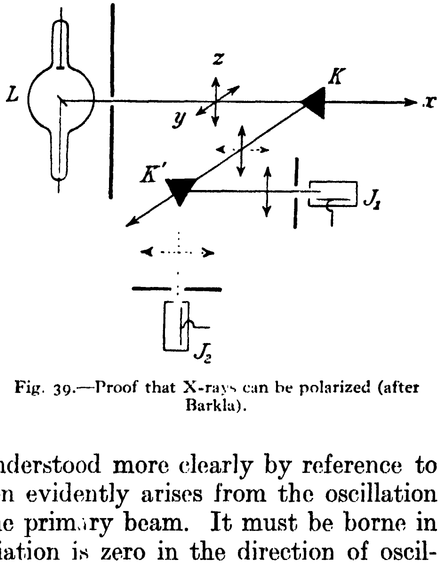

Fig. 39.—Proof that X-rays can be polarized (after Barkla).

The above result may be understood more clearly by reference to fig. 39. The scattered radiation evidently arises from the oscillation of electric charges caused by the primary beam. It must be borne in mind that the intensity of radiation is zero in the direction of oscillation (Vol. III, p. 624). In fig. 39 LK is the direction of the primary unpolarized beam, which we may regard as made up of two beams of equal intensity polarized at right angles to one another so that their electric vectors are in the directions y and z. In the interior of K the electrons are caused to oscillate in these directions and hence to emit the scattered radiation. If we observe in the direction y, we get no intensity from the electrons oscillating in this direction (in general from the y-components), but the electrons oscillating in the z-direction make a maximum contribution. The radiation in the direction KK′ is thus polarized in the xy-plane, i.e. its electric vector is at right angles to this plane in the z-direction. Now when this polarized radiation passes through K′, it sets the electrons oscillating in the z-direction. Consequently the scattered radiation from K′ has zero intensity in this direction and maximum intensity in the x-direction ($K'J_1$). The fact that the intensity is zero in the z-direction thus furnishes a proof of the complete polarization accompanying scattering and hence of the transverse undulatory nature of the rays.

Even the primary "white" radiation from an X-ray tube proves to be polarized. This is easy to understand, since the electrons which are bombarding the anti-cathode and being stopped by it, in spite of their deflections, possess an average main direction of motion, namely the direction of the incident beam of cathode rays. Hence the electric vector of the radiation has a greater magnitude at right angles to this direction than along it.

The fluorescence or characteristic radiation, whether excited by cathode rays or by primary X-rays, is (in general) not polarized. Only under special conditions involving strongly asymmetrical binding of the radiating atom can polarization be detected (J. Stark, 1930).

Spectral Distribution of Primary Continuous X-rays.—In general the X-rays given by a generating tube consist of a continuous range of wave-lengths (like white light, hence the name "white" radiation).

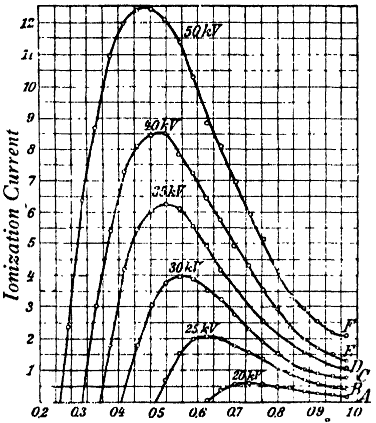

Fig. 40.—Energy distribution of "white" X-rays for different potentials

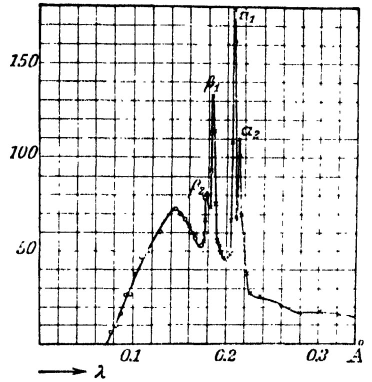

Fig. 41.—Energy distribution of "white" X-rays with superimposed characteristic X-rays. Same material as fig. 40, but with maximum potential 168 kilovolts (λ_0 = 0·073 Å.).

This is shown in fig. 40. If, however, the wave-length region in question happens to include the characteristic lines of the substance of the anti-cathode, these lines are superimposed upon the continuous spectrum (see fig. 41).

The "white" radiation is produced by the retardation of the electrons on passing into the anti-cathode. Fourier analysis of the retardation process leads to certain conclusions as to the distribution in the continuous spectrum, but actually a fundamentally different fact is observed: *the continuous spectrum possesses a clearly defined short-wave limit, whose absolute position depends upon the maximum velocity of the electrons in question.*

Measurements show that the relation between maximum electron velocity (i.e. maximum electron energy) and the frequency of the short-wave limit can be expressed by the equation (W. Wien, 1907)

$$h\nu = eU \times 10^7,$$

where $h = 6{\cdot}55 \times 10^{-27}$ erg. sec., ν is the frequency in sec.$^{-1}$, U is the electron volt-velocity, and e the electronic charge $1{\cdot}59 \times 10^{-19}$ coulomb. Since $\lambda = c/\nu$, where c is the velocity of light (3×10^{10} cm. sec.$^{-1}$), we may write

$$\lambda = \frac{12346 \times 10^{-8}}{U} \text{ cm.} = \frac{12346}{U} \text{ Å.U.}$$

Thus the short-wave limit of the continuous X-ray spectrum lies at 1 Å.U. ($= 10^{-8}$ cm.) for an electron velocity of 12,346 volts.

The quantities in the above equation can be so precisely measured that it furnishes a very good method for determining the quantity h (known as *Planck's* constant*) which, as we shall see later, is a universal constant of the greatest importance.

Reversal of the Frequency-Energy Relation.—It has already been stated above that X-rays cause the ejection of photo-electrons from atoms. As may be seen from cloud-track photographs, these photo-electrons possess a considerable velocity, which when monochromatic X-rays are used has a well-defined value. It has been found that this value is also governed by the above relationship, i.e. we have

$$\tfrac{1}{2}mv^2 = eU \times 10^7 = h\nu,$$

where v is the velocity in centimetres per second, and U the volt velocity.

From this it follows that *the fastest photo-electrons liberated by X-rays have the same velocity as the fastest electrons participating in the production of the X-rays.*

Intensity of the "White" Radiation.—At constant electron velocity this intensity is proportional to the primary electron current. At constant electron current the intensity increases rapidly with the electron velocity (approximately according to a quadratic or cubic law). The spectral distribution of the continuous or "white" radiation is independent of the substance of the anti-cathode; but the intensity at any wave-length increases in proportion to the atomic number of the anti-cathode substance when other conditions are kept constant.

Quantitative Relationships for Absorption and Scattering.—When a parallel beam of monochromatic X-rays passes through a layer of matter of thickness d, the incident intensity I_0 is reduced to the value $I = I_0 e^{-\mu d}$, where e is the base of natural logarithms and μ is a constant whose value depends upon the absorbing material and the wave-length of the X-rays. This diminution of intensity is due to absorption (causing fluorescence radiation, photo-electric effect, &c.) and to scattering.* Thus μ may be regarded as made up of two parts, $\mu = \tau + \sigma$, where τ is the **absorption coefficient** and σ the **scattering coefficient.** It is usual to refer these coefficients to unit mass by dividing by the density ρ. Thus we have

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* **Max Planck, born 1858 at Kiel, after 1889 Professor at Berlin University, was awarded a Nobel Prize in 1918.**

$$\frac{\mu}{\rho} = \frac{\tau}{\rho} + \frac{\sigma}{\rho}.$$

As a rule what is actually measured is μ/ρ, the **total mass absorption coefficient.** This is the diminution of intensity when a beam of X-rays of unit cross-section passes through unit mass of the material. It has been found that the mass absorption coefficient of an element is independent of its state of chemical combination, i.e. that the absorption is an atomic property. Hence use is often made of the so-called *atomic* absorption coefficient $\mu_{at} = (\mu/\rho) \times (A/N)$, where A is the atomic weight in question and N is Avogadro's number.

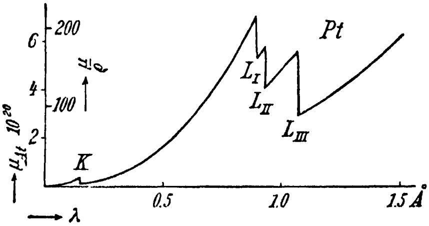

Fig. 42.—Diminution of intensity of X-rays in platinum (Z = 78) as a function of the wave-length (after Compton)

The magnitude of μ/ρ varies very greatly with the *wave-length.* Fig. 42 gives, as an example, the values for platinum. A very remarkable fact is that discontinuous variations of the absorption coefficient occur at the short-wave limit of the spectral region where K-, L- and M-emission (p. 56) take place. (For the explanation of this see p. 292.) These discontinuities of absorption are accordingly referred to as the K-edge, &c. As may be seen from fig. 42, the L-edge consists of three steps called L I, L II, and L III.

The relationship of μ_{at} and the *atomic number* is similar. Values for a wave-length of 1 Å.U. are given in fig. 43. It is important to note that a smooth curve is only obtained if the elements are arranged in the order of their *atomic numbers* (and not of their atomic weights). This was shown in particular for the elements Fe, Co, Ni, Cu by Richtmyer and Warburton in 1923.

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* In addition there are energy losses due to collisions of the X-rays with electrons (the COMPTON effect). This is only of importance for rays of very short wave-length. For further details see p. 234.

Fig. 43 shows a sudden jump in the absorption at the element whose K-edge (or L I, L II, L III edge) becomes less than 1 Å.U.

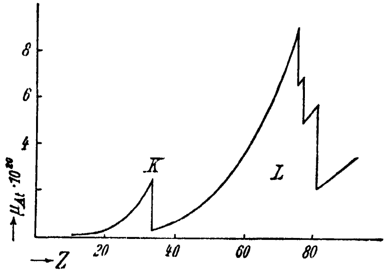

Fig. 43.—Diminution of intensity of X-rays of wave-length 1 Å. in substances with different atomic numbers Z (after Compton).

For the elements of lower atomic weight the limiting value of σ/ρ is 0·2 (up to about Z = 30). For heavier elements σ/ρ rises to 0·7. As can be seen from the numerical data for the ordinates of figs. 42 and 43 and by reference to the equation of p. 60, scattering becomes increasingly important at short wave-lengths, where it accounts for a considerable fraction of the energy involved. For the longer wave-lengths, however, the absorption of the rays by atoms with ejection of electrons plays the chief part.

Within a *continuous* region of absorption increase the value of τ/ρ is well represented by $CZ^4\lambda^3$, where C is a constant. Thus over such a region the absorption of a definite element of atomic number Z is proportional to λ^3, and for a definite wave-length λ the absorption is proportional to Z^4. We see that elements of higher atomic number absorb X-rays of a given wave-length to a very much greater extent than elements of lower atomic number (provided that the wave-length in question is not near an absorption edge).

Practical Applications of X-ray Absorption. — The medical and technical applications of X-rays for the examination of the interior of opaque substances depend upon the above fact. In these applications the rays are made to pass through the material under investigation and the shadow produced is observed, either photographically or upon a fluorescent screen. As in all cases of shadow formation, the sharpness of the shadows increases as the source is made more nearly equivalent to a point, i.e. the smaller and farther away it is.

The greater the difference between the absorption coefficients of the main substance and of the foreign body embedded in it, the greater is the contrast in the shadow image. Hence from what we have said above it is clear that the results depend chiefly upon the chemical nature of the materials used; the greatest absorption (deepest shadow) is given by the elements of highest atomic number. This is why bones, which contain calcium (Z = 20), give deeper shadows than ordinary tissue in medical X-ray photographs (see fig. 44). If it is desired to obtain shadow photographs of organs which do not themselves absorb sufficiently strongly, they are first filled with substances containing atoms of high atomic number (bismuth or barium). The absorption coefficient also increases with increasing wave-length. Hence in order to get conveniently short exposures it is necessary to choose sufficiently short wave-lengths. The range used in medical diagnostic work is about 0·48 to 0·76 Å.U. In the testing of metals for flaws the potential difference used in generating the X-rays must be chosen roughly as follows: for aluminium (up to 10 cm. thick) about 100,000 volts; for iron and brass (6 cm. thick) 200,000 to 230,000 volts. For thicker pieces of metal the still shorter γ-rays from radioactive preparations have occasionally been used.

The spectral composition of a beam of X-rays may be modified by the introduction of an absorbing screen. As the absorption increases in proportion to λ^3, the filtered rays will contain a much smaller proportion of the longer wave-lengths, and will therefore as a whole be rendered more nearly homogeneous. By making suitable use of the marked discontinuities in the absorption curves of the screen substances, it is possible to filter out very narrow spectral regions without too great a reduction of intensity.

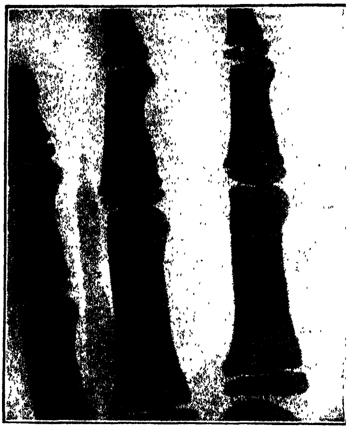

Fig. 44.—Variation of absorption of X-rays with the atomic number (Ca and P in bones, as compared with C, H, and O in flesh).

The Number of Scattering Electrons.—We may imagine that when X-rays, which consist of electromagnetic waves, pass through matter, the electrons in the atoms are made to oscillate in step with the oscillating electric field, just as in the case of long electric waves. Each oscillating electron thus becomes the source of new waves of the same wave-length, which pass out from it in all directions. In other words, the incident rays are scattered. If a number of electrons are affected simultaneously by the incident wave, special considerations arise. In the case of long waves all the electrons oscillate coherently, i.e. in phase, within a region comparable with the wave-length. For visible light the electrons of any given molecule oscillate coherently, but not the electrons of different molecules. For the very short waves of X-rays the electrons within a single atom may be regarded as individuals, i.e. behave incoherently. Hence the intensities of the scattered waves sent out from them may be added together, whereas in the case of coherently oscillating electrons the field strengths must be added and interference phenomena arise.

According to Maxwell's classical theory, the energy radiated in unit time by an accelerated charge of e electrostatic units is given by

$$S=\frac{2}{3}\frac{e^2}{c^3}\left(\frac{dv}{dt}\right)^2.$$

Here dv/dt is the acceleration of the electron, which is proportional to the electric field strength E_i of the incident waves, i.e. $m\,dv/dt = -eE_i$, provided that the electron may be treated as if it is free and the forces binding it to the atom are negligible.

With this proviso we obtain the following value S_s for the energy scattered in unit time by the electrons of the n atoms contained in a unit cube of the substance:

$$S_s = \frac{2}{3}\frac{e^2}{c^3}\left(\frac{dv}{dt}\right)^2 nZ = \frac{2}{3}\frac{nZe^4E_i^2}{m^2c^3},$$

where Z is the number of electrons per atom. The energy S_i of the incident rays per unit area and unit time is $S_i = cE_i^2/(4\pi)$. The ratio S_s/S_i is the absorption coefficient of the substance in question, hence

$$\sigma = \frac{S_s}{S_i} = \frac{8\pi e^4 nZ}{3m^2c^4}.$$

Putting the density ρ equal to nA/N, where A is the atomic weight and N is Avogadro's number, we obtain

$$\frac{\sigma}{\rho} = \frac{8\pi e^4 NZ}{3m^2c^4A} = K\,.\,\frac{Z}{A}.$$

The value of K comes out as 0·4.

Now it has already been stated that $\sigma/\rho = 0{\cdot}2$ for the lighter elements (for which the neglect of the binding forces is more or less permissible, p. 61). Hence it follows that $Z/A = 0{\cdot}2/0{\cdot}4 = \frac{1}{2}$, i.e. *the number of scattering electrons in an atom is (for the light elements) about half the atomic weight.*

This result, obtained by J. J. THOMSON in 1906, had a very important bearing on subsequent theories of the structure of matter (p. 82).

12. Scattering of X-rays by Centres occurring at Regular Intervals

Crystals as Gratings.—When X-rays are scattered by centres arranged at regular intervals, interference phenomena similar to those observed with ordinary light and gratings may occur. It has already been mentioned in Vol. IV (p. 209) that X-rays give the same diffraction effects as visible light when incident on a grating, provided that the angle of incidence is sufficiently large. An alternative method of obtaining interference effects with X-rays is to choose a grating with a very much smaller constant, corresponding to the shorter wave-length of X-rays as compared with visible light.

In this connexion LAUE, in 1912, suggested an idea destined to be one of the most fruitful in modern science. He pointed out that suitable gratings lie ready to hand in crystals, in which the regular spacing of the constituent atoms is comparable with the wave-length of X-rays.

It had always been a cherished belief with mathematicians and mineralogists that the external symmetry of crystals was due to a regular internal arrangement of molecules. Once we knew how to calculate the number of molecules per unit mass (Vol. II, p. 53), it became possible to estimate their distance apart. We may consider a cube of copper of 1 cm. edge and imagine the atoms to be arranged at equal distances apart. Then we may divide up the cube into a large number of tiny cubes, each containing one atom. If N is the number of atoms in a gramme-atom, A the atomic weight, and ρ the density, the volume of a gramme-atom is A/ρ and the volume of each of our tiny cubes is $A/(\rho N)$. The length a of the side of the tiny cube is $\sqrt[3]{A/(\rho N)}$. In the case of copper, for example, we have $A = 63{\cdot}57$, $N = 6{\cdot}06 \times 10^{23}$, $\rho = 8{\cdot}9$ gm./cm.^{3}. Hence we obtain $a = 2{\cdot}3 \times 10^{-8}$ cm. Similar values are obtained for other substances, even if we consider other arrangements of the atoms, which of course are not always distributed regularly in cubes as assumed above.

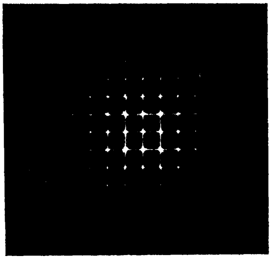

Fig. 45.—Diffraction pattern seen when a distant monochromatic point-source is viewed through two linear gratings superimposed at right angles.

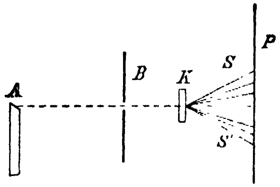

Fig. 46.—Diagram of apparatus used by Friedrich and Knipping, on Laue's suggestion, to demonstrate the diffraction of X-rays. A = anticathode, B = slit, K = crystal, P = plate, S and S′ = diffracted rays.

We see that the distance between the atoms in crystals is of the same order of magnitude as the wave-length of X-rays as determined e.g. by diffraction experiments with slits. If then the atoms are really arranged as regularly as is suggested by the external regularity of the crystals, diffraction effects must occur when X-rays pass through crystals, just as diffraction effects are observed when light passes through linear gratings, that is, the ordinary ruled gratings, or two-dimensional gratings (e.g. if we look at a distant source of light through a fairly loosely woven cloth (fig. 45)). On this principle, but with a three-dimensional grating instead of a two-dimensional, depends the apparatus used by **Friedrich** and **Knipping** (1912) at **Laue's** suggestion. A narrow beam of " white " X-rays, after passing through suitable apertures in lead screens B (fig. 46), falls upon the crystal K. Behind the crystal and not too far away from it is placed a photographic plate P. Fig. 47 shows one of the first successful photographs, which was obtained by passing the X-rays through a thin plate of zinc blende in the exact direction of the crystal axis. In the middle is the point of incidence of the primary beam, which is recorded as a heavily blackened spot. Around this lie a number of much feebler spots distributed with fourfold symmetry (corresponding to the symmetry of the crystal axis). These spots, which lie on straight lines passing through the central point, correspond in part to the spectra of different orders, and their intensity falls off rapidly as the ordinal number increases. The different groups of spots also correspond to different wave-lengths in the X-rays, as we shall now explain in greater detail.

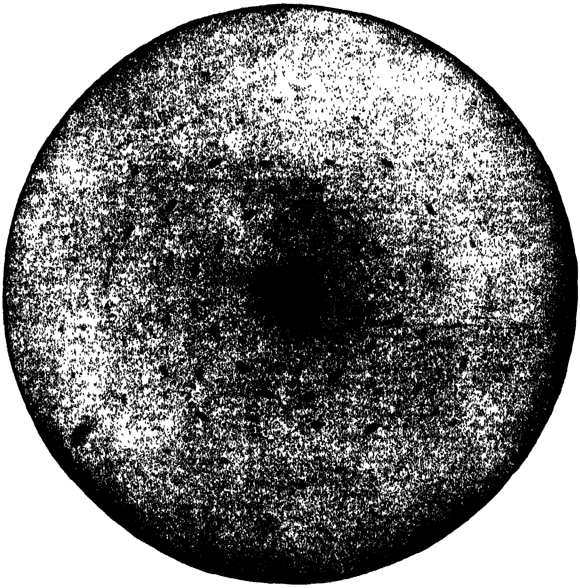

Fig. 47.—Laue pattern for X-rays passing through a ZnS crystal parallel to the axis

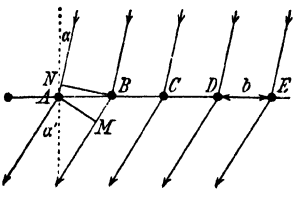

Fig. 48.—Diffraction by a linear grating

Calculation of the Interference Pattern given by a Three-dimensional Grating.—We shall confine ourselves to the case of parallel rays, as this suffices for an understanding of the underlying principles. We begin by considering the phenomena of diffraction by an ordinary linear grating in a somewhat more general way than we did in Vol. IV, p. 205. The points of fig. 48 represent the diffraction centres (e.g. the intersections of the spaces of the grating with the plane of the paper).

The rays shown will reinforce one another in those directions for which the path difference of neighbouring rays is a whole wave-length or a whole number of wave-lengths. Let α and α' be the angles of incidence and diffraction respectively (the angles with the normal) and b the spacing constant of the grating. Draw BN perpendicular to NA and AM perpendicular to MB (see fig. 48). Then the path difference between neighbouring rays after diffraction is clearly $BM - NA = b \sin \alpha' - b \sin \alpha$. Hence reinforcement and maximum intensity in the diffraction pattern will occur when

$$b(\sin \alpha' - \sin \alpha) = n\lambda,$$

where n is an integer. If, on the other hand, $n = \frac{1}{2}$ or an odd multiple of $\frac{1}{2}$, interference will occur and a minimum of intensity will result.

A two-dimensional array of points (double grating) may in the simplest case be regarded as a periodic repetition of the one-dimensional grating in a plane (fig. 49). We now think of a beam incident upon this two-dimensional array at an oblique angle to the plane of the figure. Behind this plane there will be points of reinforcement where the path differences from all the openings are integral multiples of a wave-length. Hence if α and α' are the angles of incidence and diffraction respectively, referred to the x-axis of the grating, and β and β' the corresponding angles referred to the y-axis, the conditions for reinforcement are

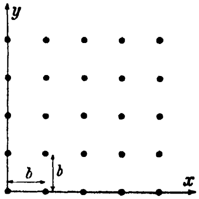

Fig. 49.—Square double grating

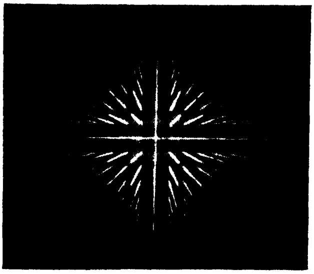

Fig. 50.—Diffraction spectra of white light produced by a double grating

$$b(\sin \alpha' - \sin \alpha) = n_1\lambda,$$
$$b(\sin \beta' - \sin \beta) = n_2\lambda.$$

The combination of these two equations gives a double array of spectra, as shown in fig. 50. If the light is monochromatic, so that there is only one value of λ, the diffraction pattern consists of a number of points (see fig. 45).

We now pass on to a three-dimensional array of scattering centres (fig. 51), confining our attention to the simple cubic case where the spacing constant b is the same in all three directions. Here we have three conditions for diffraction maxima:

$$b(\sin\alpha' - \sin\alpha) = n_1\lambda,$$
$$b(\sin\beta' - \sin\beta) = n_2\lambda,$$
$$b(\sin\gamma' - \sin\gamma) = n_3\lambda.$$

We may solve these equations for $\sin\alpha'$, $\sin\beta'$, $\sin\gamma'$, and then square and add, remembering that

$$\sin^2\alpha + \sin^2\beta + \sin^2\gamma = 1$$

and

$$\sin^2\alpha' + \sin^2\beta' + \sin^2\gamma' = 1.$$

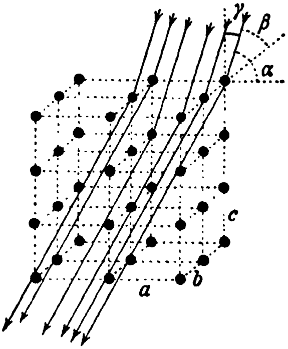

Fig. 51.—Diffraction of X-rays by a space lattice

In this way we obtain the following result:

$$1 = 1 + 2(n_1 \sin\alpha + n_2 \sin\beta + n_3 \sin\gamma)\frac{\lambda}{b} + \left(n_1^2 + n_2^2 + n_3^2\right)\frac{\lambda^2}{b^2},$$

whence

$$\lambda = -\frac{2b(n_1 \sin\alpha + n_2 \sin\beta + n_3 \sin\gamma)}{n_1^2 + n_2^2 + n_3^2}.$$

Since n_1, n_2, n_3 are small integers (the spectra of higher order being very feeble), we see that for an interference maximum to occur when the angle of incidence is given, the wave-length must have a perfectly definite value (or one of a few definite values). Thus the rays diffracted by the space lattice for this given angle of incidence do not contain all the incident wave-lengths, but only certain definite wave-lengths. For a given angle of incidence the rays diffracted in a certain direction have a perfectly definite wave-length. If 2θ is the angle between the incident ray and the diffracted ray, then, by an elementary formula of Solid Geometry,

$$\cos 2\theta = \sin\alpha \sin\alpha' + \sin\beta \sin\beta' + \sin\gamma \sin\gamma'.$$

Hence, on squaring and adding the original equations we finally obtain

$$\sin\theta = \frac{\lambda}{2b}\sqrt{n_1^2 + n_2^2 + n_3^2}.$$

If the lattice spacing is different in different directions (a, b, c) in space and if the axes of the lattice are inclined to one another, the expression also involves the spacing constants a, b, c and the mutual inclinations of the axes.

We see that the different spots in the Laue photograph of fig. 47 correspond to different wave-lengths. Hence in the Laue method it is necessary to use " white " X-rays (a continuous spectrum, containing a range of wave-lengths). The interference effects at the lattice then select quite narrow wave-length regions for the building of the pattern, which thus depends on the structure of the crystal used.

So-called Reflection of X-rays.—The above phenomena may be regarded somewhat differently (as was done by W. H. Bragg and W. L. Bragg,* 1913). The space lattice may be looked upon as a succession of planes, the planes in which the lattice points are situated (see fig. 16, Vol. I, p. 274).

We now consider a parallel beam of monochromatic X-rays incident upon a succession of planes at the glancing angle α. Diffraction occurs at the scattering points lying in the planes. The maximum intensity from any single plane is in the direction corresponding to ordinary reflection of the beam. Two successive planes are shown in fig. 52, the respective points of incidence of two rays being A_0 and A_1. These two points are chosen so as to lie on the normal to the two planes, so that the distance A_0A_1 is equal to d, the spacing constant. Both the rays undergo the reflection just referred to, and if we assume that the refractive index is unity, the path lag of the second ray relative to the first after leaving the planes is

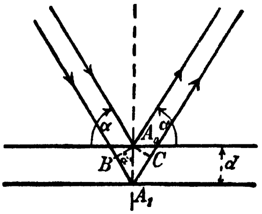

Fig. 52.—Reflection at lattice planes

$$BA_1 + A_1C = 2A_1C = 2A_0A_1 \sin\alpha = 2d \sin\alpha.$$

The rays reinforce one another when this path difference is an integral number of wave-lengths. Hence the *reflection* from the whole succession of planes must take place at certain perfectly definite angles. These angles for which an incident beam is regularly reflected with maximum intensity are given by the equation (the *Bragg relation*)

$$2d \sin\alpha = n\lambda,$$

where n is an integer. The greater the number of planes, the sharper are the maxima and the more nearly monochromatic are the rays reflected at a given angle, since the neighbouring wave-lengths cancel one another by interference. This is analogous to the case of an ordinary linear grating, for which the sharpness of the spectral lines increases with the number of rulings.

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* Sir William H. Bragg (1862–1942) became Professor at Adelaide University in 1886, at Leeds in 1909, and in London in 1915; later Director of the Royal Institution, London. He was awarded the Nobel Prize (together with his son W. L. Bragg) in 1915 for work on X-rays and crystal structure, and was knighted in 1920.

W. L. Bragg, born in 1890 at Adelaide, became Professor of Physics at Manchester University in 1919, Director of the N.P.L. in 1937, and Cavendish Professor at Cambridge in 1938.

Thus when " white " radiation falls on a space lattice (or a regular succession of reflecting planes) at a given angle of incidence, only one wave-length (or rather, one set of wave-lengths, obtained by putting $n = 1, 2, 3, \ldots$ in the above equation) is reflected. If the incident radiation is monochromatic, then reflection occurs only at one angle (or rather, one set of angles).

Whereas in the optical case these phenomena are only realized in the experiment described in Vol. III, p. 643, the two **Braggs** have shown that with X-rays the phenomena occur in every reflection at a crystal face, owing to the penetration of the X-rays into the interior of the substance in question.

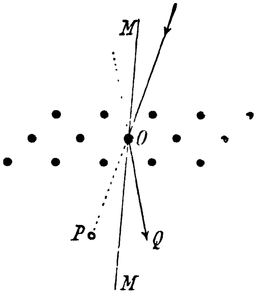

Fig. 53.—To illustrate the derivation of the Bragg condition from the diffraction at a space lattice.

It can easily be shown that this reflection condition is identical with the conditions obtained above in the discussion of diffraction, i.e. that the mean plane M between the incident ray and any possible diffracted ray (see fig. 53) must always be a lattice plane (Vol. I, p. 274).

Let O be the origin of a system of rectangular co-ordinates with its axes in the directions of the crystal axes of the cubic crystal under consideration, and let the points P and Q be at unit distance from O. Then, if we use the notation of the previous pages, their co-ordinates are ($\sin\alpha$, $\sin\beta$, $\sin\gamma$) and ($\sin\alpha'$, $\sin\beta'$, $\sin\gamma'$) respectively. Let any point R in the mean plane M have the co-ordinates (x, y, z). Then since PR = QR, we have

$$(x - \sin\alpha)^2 + (y - \sin\beta)^2 + (z - \sin\gamma)^2$$
$$= (x - \sin\alpha')^2 + (y - \sin\beta')^2 + (z - \sin\gamma')^2$$

or

$$x(\sin\alpha' - \sin\alpha) + y(\sin\beta' - \sin\beta) + z(\sin\gamma' - \sin\gamma) = 0.$$

Substituting the diffraction conditions $b(\sin\alpha' - \sin\alpha) = n_1\lambda$, &c., we obtain

$$n_1x + n_2y + n_3z = 0.$$

This equation expresses the fact that any plane parallel to M cuts off intercepts on the crystal axes inversely proportional to the integers n_1, n_2, n_3 respectively. But this means that M is a lattice plane. Suppose that p is the greatest common factor of n_1, n_2, n_3, so that $n_1 = ph$, &c. The numbers h are called the *crystallographic indices* (Miller indices) of the plane M, and are used in crystallography to determine this plane. Now the distance d between two successive lattice planes parallel to a plane with the indices h_1, h_2, h_3 is given by

$$\frac{1}{d} = \frac{1}{b}\sqrt{h_1^2 + h_2^2 + h_3^2},$$

where b is the spacing constant. Substitution of this in the final equation on p. 67 gives **Bragg**'s reflection relation.

The X-ray Spectrometer—The fact that the "reflection" angle depends on the wave-length can be used for the spectral analysis of X-rays. The beam, restricted in cross-section by passages through successive slits in lead screens, is allowed to fall on the crystal, which is then rotated so as to vary the angle of incidence. The reflected beam for any position of the crystal contains only those wave-lengths which satisfy the Bragg relation. Hence as the crystal is rotated the different wave-lengths are reflected at different angles and produce separate images on a suitably placed circular photographic film (see fig. 54). As is the case with grating spectra of ordinary light, the lines of the different orders may overlap. Instead of the photographic film an ionization chamber with a slit may be used. The crystal may then be kept at rest and the chamber rotated to successive positions so that the different wave-lengths fall on its slit (**ionization spectrometer**).

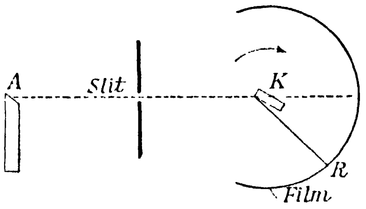

Fig. 54.—Diagram to illustrate the rotating crystal method

In order to determine the spectral composition of a beam of X-rays in this way, it is necessary to know the type of the crystal lattice and the lattice spacing. Conversely, if the wave-length of the X-rays is known, the angle of reflection may be used to determine the lattice spacing.

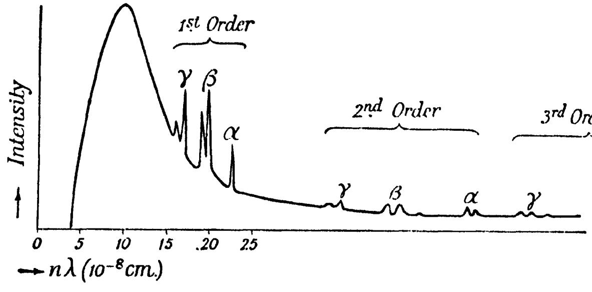

Fig. 55.—Rotating crystal record obtained with ionization chamber. L-series of tungsten (40 kilovolts) and a calcite crystal

Fig. 55 shows a record obtained with an ionization chamber and self-registering electroscope (A. H. Compton). The continuous background with its sharp limit on the short-wave side can be seen; also the fall of intensity towards longer wave-lengths, which is due mainly to absorption in the glass of the tube. Superimposed on these are the characteristic radiations of the tungsten anti-cathode: several lines of the L-series appear in the figure. In order to get the lines of the K-series

(p. 73), which have much shorter wave-lengths, it is necessary (see the relation given on p. 59) to use a potential of at least 75 kilovolts to accelerate the electrons in the tube (fig. 40, p. 58).

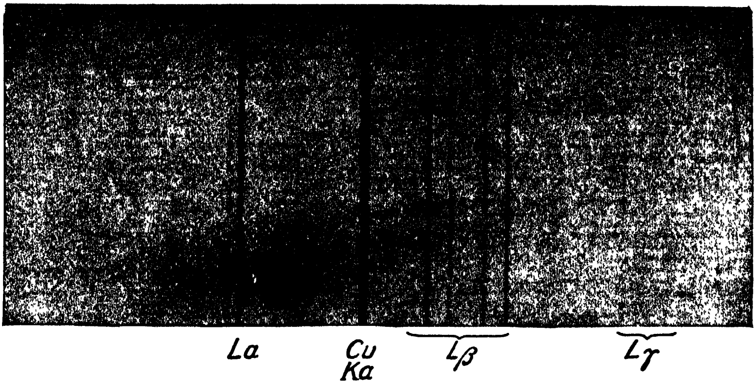

Fig. 56.—Portion of X-ray spectrum obtained by the rotation method. The L-series of ytterbium

[From Siegbahn, *Spektroskopie der Röntgenstrahlen* (J. Springer, Berlin).]

Now that we know how to produce X-rays of great intensity by easily controllable means, the photographic method is used almost exclusively. The ionization chamber method is still used, however, for accurate measurements of intensity.

Fig. 56 shows a portion of an X-ray spectrum obtained by the **rotating crystal method.** In practice a narrow beam, passing through slits in lead screens, is generally used; to obtain greater intensities, however, a divergent beam may also be employed, but in this case the film must be in a quite definite position. This focussing condition is as follows. The film and the entrance slit must lie upon a circle whose centre is on the axis of rotation of the crystal (see fig. 57). If this is so, then even with a divergent beam rays of a definite wave-length only can strike any given point of the film. Thus when the crystal is in the position K (fig. 57), the ray shown as a continuous line is reflected to C; when the crystal comes to the position K′, the ray (of the same wave-length) shown by a dotted line is reflected to the same point of the film. The Bragg condition is fulfilled in both cases; for all the angles subtended by the chord SC at the circumference of the smaller circle of the figure are equal, and the angle between MK and MK′ is equal to that between the two rays in question.

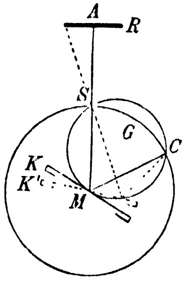

Fig. 57.—Focussing (condition) in the rotation method.

The Bragg principle may be applied in other ways. Thus fig. 58 is a diagram of Seemann's so-called **knife-edge method.** The slit is practically on the crystal surface, so that only the portion of the crystal in the immediate neighbourhood of the knife-edge is effective. The crystal may therefore be very small. In the case of very hard X-rays (i.e. very penetrating X-rays, or rays of very short wave-length) the beam may be allowed to pass directly through the crystal (fig. 59), use being made of the reflections at the internal lattice planes (represented by the horizontal lines of the figure).

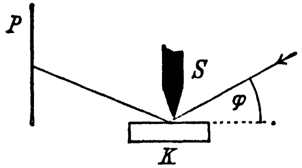

Fig. 58.—Seemann's knife-edge method

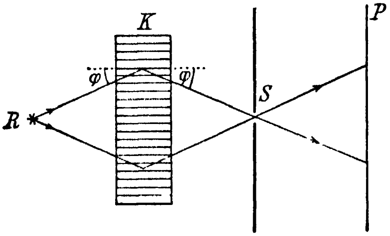

Fig. 59.—Reflection at internal planes (Rutherford and Andrade)

These are the methods by which the wave-lengths of γ-rays (p. 21) have been determined.

Reflection at Different Crystal Faces.—In any crystal there are various sets of lattice planes with different spacings (see fig. 16, Vol. I, p. 274). Hence spectra of different appearance may be obtained with the same crystal and the same X-rays, according to the angles which the crystal surfaces make with the crystallographic axes. For instance, a rock-salt crystal (which is usually bounded by cubic planes of its lattice) may be ground down to an octahedral or dodecahedral form. As we see at once from the figure just referred to, however, the density of lattice points on planes separated by small distances is less than in planes which are farther apart, and the diffraction effects are accordingly less intense.

The Debye-Scherrer Method.—Instead of rotating a single crystal, it is possible to use a large number of very small crystals arranged at random (the so-called **powder method**) The powder contains crystals pointing in all directions, so that there will always be some crystal faces inclined so as to exhibit any given type of reflection. The powder is pressed into the form of a small rod about 1 mm. thick and 10 mm. long, and this is placed along the axis of a circular camera. A narrow beam from a system of slits is then allowed to fall upon it; reflections occur at all the faces for which the Bragg condition is satisfied. In order to make sure that all possible orientations of the crystals are represented, the powder may be rotated during the exposure. The rays corresponding to any given type of reflection form a cone whose axis is the line of incidence and whose angle is twice the angle between this axis and any reflected ray.

Fig. 60 is a reproduction of a powder photograph obtained in this way. The lines are the intersections of the cones with the cylindrical film. This method is used with monochromatic X-rays to determine the crystal structure of powders.

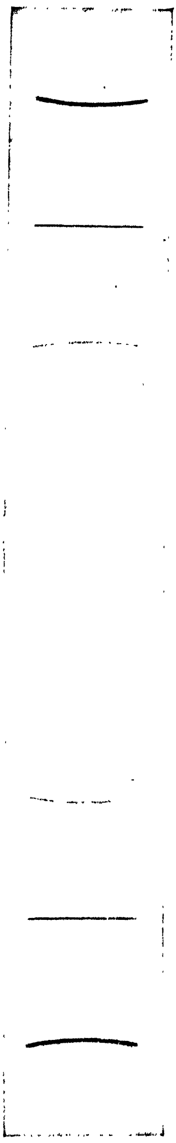

Fig. 60.—Powder spectrogram of a molybdenum wire, using a chromium anti-cathode (Debye-Scherrer method). [Seemann laboratory, Freiburg.]

13. X-ray Spectra

The above interference methods enable us to determine the crystal structure of solids if the wave-length of the X-rays used is known. This will be discussed in greater detail in Chapter VII (p. 404). Conversely, if the crystal structure is known, these methods serve to determine X-ray wave-lengths very accurately. If we apply the Bragg condition (p. 68), we have only to measure the angle at which reflection occurs. The distance d between successive lattice planes is known for many crystals (see p. 407). The maximum d-values for some commonly-used crystals are as follows:

Rock salt: $d = 2{\cdot}814 \times 10^{-8}$ cm.
Calcite: $d = 3{\cdot}029 \times 10^{-8}$ cm.
Sugar: $d = 10{\cdot}572 \times 10^{-8}$ cm.

Melissic acid has the very large value $d = 73{\cdot}5 \times 10^{-8}$ cm.

The longest wave-length theoretically measurable with any given crystal is that for which the glancing angle is 90° (i.e. normal incidence). The Bragg condition then reduces to $\lambda = 2d$ for the first order. Actually for practical reasons (insufficient intensity) glancing angles greater than 60° are not used, so that the longest wave-length which can be measured is in fact much shorter. For soft X-rays mechanically-ruled gratings are therefore used (see Vol. IV, p. 209).

The spectroscopy of X-rays gives the following results. As has already been concluded from direct absorption measurements (p. 60), each element emits characteristic X-rays lying in widely separated regions referred to (in order of increasing wave-length) as K, L, M, N, &c. Each of these regions contains a number of characteristic lines, this number increasing from K onwards.

In contrast to the great differences exhibited by optical spectra, the X-ray spectra of all the elements are very similar in structure, especially in the short-wave region. Thus K-spectra chiefly consist of two lines, the strong Kα line and the weaker line of shorter wave-length Kβ. With high resolution each of these lines is found to be double or triple (the components being denoted by α_1, α_2, β_1, β_2, β_3, &c., in order of increasing wave-length). Some K-series are shown

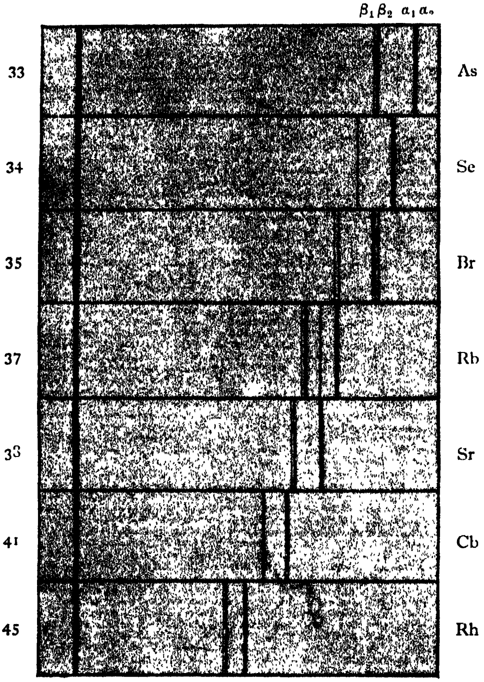

Fig. 61.—K-series

(for elements between arsenic ($Z = 33$) and rhenium ($Z = 47$)).

in fig. 61. The L-series (see fig. 62) are considerably more complicated. Here there are three main groups of lines, labelled α, β, γ as before. The M-series are still more complicated and display greater individual differences.

In connexion with the origin of these spectra the following fact is of great importance. The wave-lengths of the emitted spectra are longer than those of the corresponding absorption edges. For the excitation of a given line, e.g. a Kα line of wave-length λ_α, it is not sufficient (as might be thought from the equation given on p. 59) to use the potential $U = h\nu_a/e$. The continuous spectrum will have the short-wave limit λ_a, but the characteristic Kα line will not appear (see fig. 63). Not until the potential reaches such a value that the wave-length of the K *absorption edge* can be emitted, does the characteristic K-spectrum make its appearance. Then all the K lines appear simultaneously. The same is true for the L-series and the other series (due account being taken of the fact that there are a number of absorption steps (p. 60)). Thus in order to cause the emission of a series, the potential used must be at least that corresponding to the wave-length of the corresponding *absorption edge*.

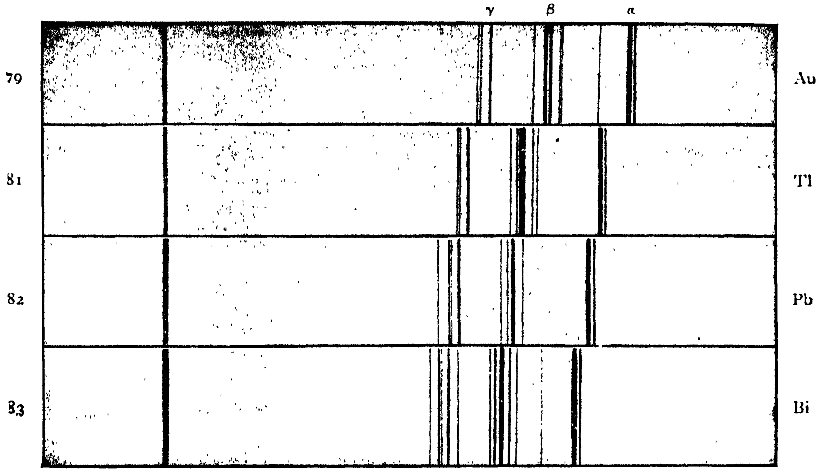

Fig. 62.—L-series

For the bearing of this fact on the theory of X-ray spectra see p. 293. Another important fact is that the different series, and also certain lines of a particular series, are only given by elements with atomic numbers above certain values. Thus, for example, the K_a line can be followed for the elements down to boron ($Z = 5$, $\lambda = 70$ Å. approx.), but the Kβ_1 line appears first for sodium ($Z = 11$) (cf. fig. 64, p. 77).

Relations between the X-ray Spectra of the Different Elements.—The different spectra reproduced in figs. 61 and 62 are all on the same scale. It is seen that there is a regular displacement of the lines towards the shorter wave-lengths as the atomic number of the element (given on the left in the figures) increases. This fundamental fact was first discovered by MOSELEY * in 1913. Fig. 64 is a diagrammatic arrangement of the spectra, which brings out the regularities very clearly. MOSELEY showed that corresponding lines (e.g. Kα lines) of the different elements had frequencies which very nearly satisfy the equation $\sqrt{\nu} = (Z - b)\sqrt{R}$, where ν is the frequency, Z the atomic number, and R and b constants (b is approximately unity). Thus if we plot $\sqrt{\nu}$ or $\sqrt{(\nu/R)}$ against Z, we obtain straight lines (fig. 65). The Moseley relationship holds particularly accurately for the K-series. The " lines " for the other series show deviations from the law, and these deviations are of great significance in the theory of atomic structure. This will be discussed more fully on p. 297. The investigations of MOSELEY are of fundamental importance from several points of view. In the first place they showed that a regular sequence of spectra is only obtained when the elements are arranged in the order of *atomic number*, and not in the order of atomic weight. This provides strong support for the order of the elements in the periodic classification, based on chemical properties, &c., which also shows deviations from the order of atomic weight, e.g. in the cases of I — Te, A — K, Co — Ni. In addition to this, MOSELEY'S experiments for the first time made it possible to predict the existence of elements as yet undiscovered. These predictions have since been verified in a number of cases, e.g. hafnium, rhenium, and masurium. The elements 61, 85, and 87 have not yet been discovered for certain. The Moseley relation furnishes an extremely important and very accurate method of detecting such new elements, since it is possible to calculate the positions of the X-ray lines of the unknown element easily and accurately from those of the neighbouring known elements. Extremely small quantities of material placed on the anticathode of an X-ray tube suffice for a determination of the characteristic X-ray frequencies, and so the presence of a new element may be detected even when it is present in such small quantities that direct chemical methods cannot be applied. The full significance of MOSELEY'S

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* H. G. J. MOSELEY (1887–1915) worked at Manchester under RUTHERFORD and later at Oxford; he was killed at Gallipoli on 10th August, 1915.

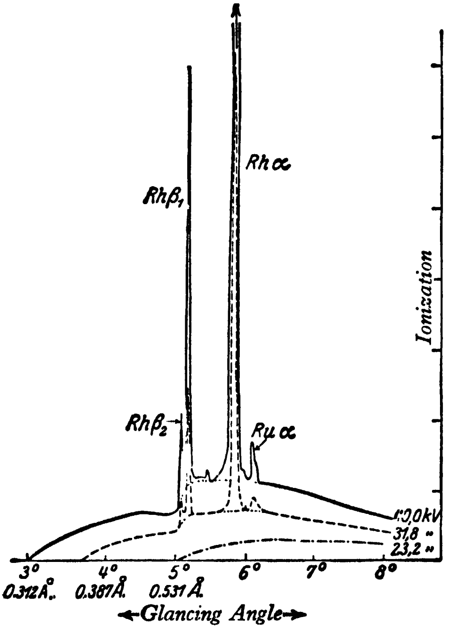

Fig. 63.—Relation of K-emission to the exciting potential (after Webster)

[From *Handbuch der Experimentalphysik*, Vol. XXIV, 2 (Akademische Verlagsgesellschaft, Leipzig).]

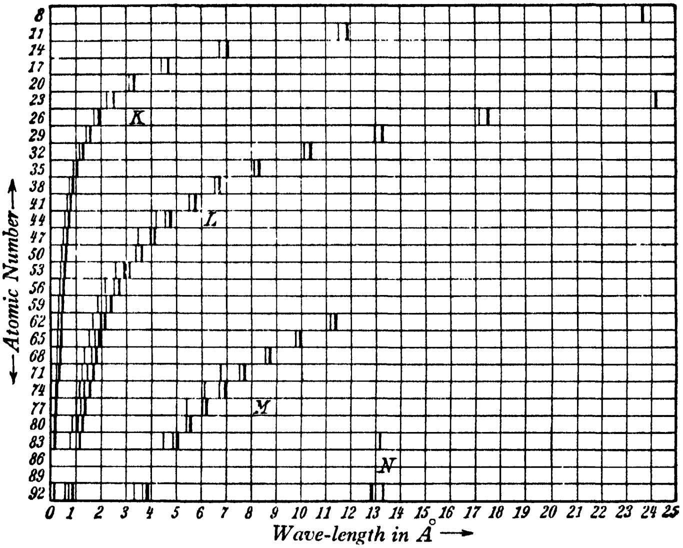

Fig. 64.—The principal X-ray lines of the different elements

[From *Handbuch der Experimentalphysik*, XXIV, 2]

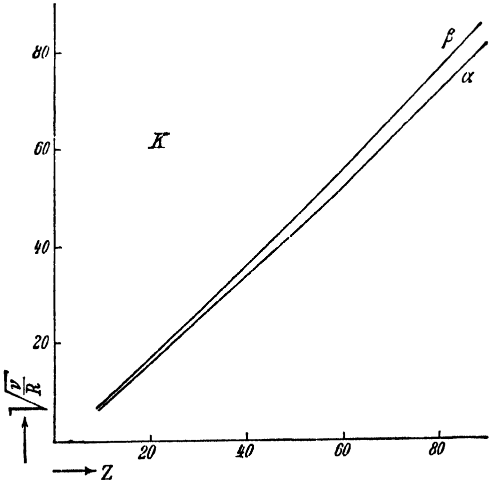

Fig. 65.—Graph of $\sqrt{\nu/R}$ for the K-series as a function of the atomic number Z

law (in particular the meaning of the numerical values of the constants), however, will not be apparent until later (p. 294).

Absorption Spectra. — The spectral investigation of absorption presents no new features and may be carried out by the photographic or ionization methods already mentioned. One peculiarity of the photographic method is that the silver and bromine in the photographic emulsion give their own absorption, so that all photographs (p. 169) in which the continuous spectrum is sufficiently strong exhibit a discontinuity of absorption (the absorption becoming stronger on the short-wave side of the absorption edges). From the point of view of the energy involved, the beginning of increased absorption at an absorption edge is easily understandable (p. 135); for all the rays with wave-lengths lower than the absorption edge use up a certain amount of their energy in exciting the emission of the corresponding characteristic lines. This is illustrated in fig. 66.

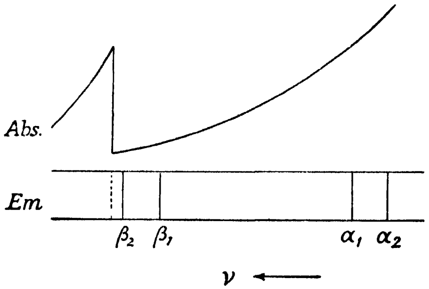

Fig. 66.—Relation between absorption and emission for an X-ray series

E. The Passage of α-rays through Matter

14. Absorption and Formation of Ions

Besides electrons and electromagnetic waves (see above), we may also use corpuscular rays (e.g. canal rays) for investigating the structure of matter. Radioactive substances form an important source of such particles travelling at high speeds, namely, the α-rays (helium atoms with a double positive charge). As we have already stated on p. 17, the α-particles from any given radioactive change have a well-defined velocity, and their high power of penetration through matter makes them very suitable for investigations of structure. In what follows we shall confine ourselves to the results of experiments with α-particles.

The Absorption of α-particles.—As was mentioned on p. 17, α-particles lose their energy as they pass through matter and can only travel certain distances. It is a very remarkable fact that the number of α-particles penetrating through different thicknesses of a material medium remains practically constant up to a certain thickness (the so-called *range*), at which it then rapidly falls off to zero. This can be verified experimentally by counting the number of scintillations produced per minute on a screen by a beam of α-rays in air, the screen being placed successively at different distances from the source and due account being taken of the change in the solid angle subtended by the screen at the source. Cloud-chamber photographs of α-ray tracks also show the very definite value of the range directly (see fig. 6, p. 19).

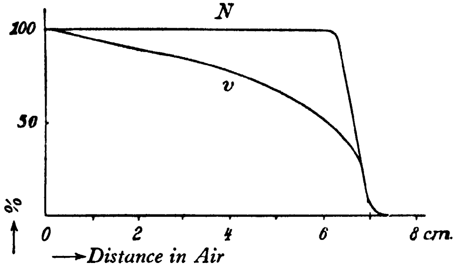

Fig. 67.—Range of α-particles of RaC′ in air (curve N) and variation of velocity with distance (curve v)

The curve N of fig. 67 represents the percentage of α-particles penetrating different thicknesses of air at 0° and 760 mm. pressure. The particles in question are from a RaC′ source. The range is defined as the point at which the steep fall of the curve would cut the axis when produced. In the present case the range is 6·97 cm. The corresponding curves for the α-rays from other sources are obtained by simply displacing the zero of the axis of abscissæ. Thus for particles

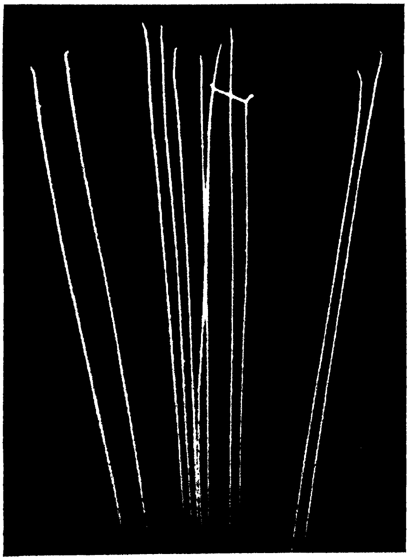

Fig. 68.—Variation of the range of α-particles

[From Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances*.]

with a range of 4 cm. the axis of ordinates must be erected at the point corresponding to 3 cm. in fig. 67. In actual fact all the particles are not affected in quite the same way in their passage through the large number of atoms in their range (for the α-particles from RaC′ this number is about ten million), and so the ranges of individual particles vary slightly. This is shown in fig. 68 (magnified about 2½ times).

The range of α-particles in air is reduced by placing a thin layer of some solid material in their path. This effect is expressed in terms of the corresponding distance in air at 0° C. and 760 mm. pressure, i.e. the thickness of air which has the same stopping power as the solid in question. For example, an aluminium foil 0·001 mm. thick is equivalent to 0·17 cm. of air. For the slower α-particles the air equivalent depends upon the initial velocity. Some numerical values are given in Table IX for α-rays with a range of 6 cm. (corresponding to an initial velocity of $1{\cdot}84 \times 10^9$ cm./sec.). As α-rays pass through matter the velocity v falls off with increasing distance. This has been proved by the deflection of the α-rays in a magnetic field and also by calorimetric measurement of the heating effect (Kapitza, 1923). The curve marked v in fig. 67 shows the effect graphically. The so-called Geiger relation

TABLE IX

Material	Mg./cm.² equivalent to 1 cm. Air at 15° C.	Thickness in mm.
Al	1·62	0·006
Cu	2·26	0·0025
Ag	2·86	0·0021
Pt	4·4	0·0020
Au	3·96	0·0021
Mica	1·4	0·005

$$v^3 = \mathrm{CR},$$

where R is the range and C is a constant, was thereby found to hold, at least for the higher velocities. This equation is often used to calculate initial velocities from measured ranges. Difficulties arise in experiments with slower α-particles, because they pick up additional charges. By means of magnetic deflection experiments Henderson (1922) showed that not all the α-particles remain as helium atoms with a double positive charge (He^{++}) throughout the whole of their flight, but that a certain fraction become He^{+} and (at low velocities) neutral helium. The more detailed investigations of Rutherford have proved that (as in the case of canal rays) repeated changes of charge take place, and that these changes are more frequent the slower the particle is.

Ionization by α-rays.—Just as in the case of cathode rays (p. 36), electrons may be ejected from atoms through which an α-particle passes. Along the track of an α-particle a dense trail of ions is formed, and these enable the track to be seen and photographed in a cloud-chamber. The total number of carriers produced by an α-particle from RaC′ over its whole range is 2·36 × 10^5. The differential ionization (in the case of α-rays usually expressed in ion-pairs per millimetre) is plotted in fig. 69.

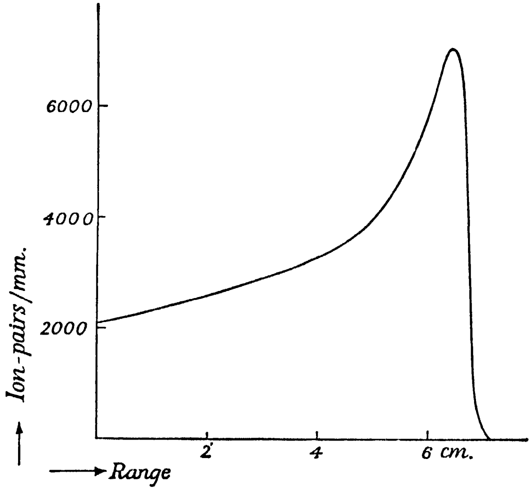

Fig. 69.—Ionization by the α-particles from RaC′. Number of ion-pairs per mm. of path in air as a function of the distance travelled

Comparison with the data for electrons of the same velocity (see Table VIII, p. 47; to apply to 1 mm. the values must be divided by 10) shows that the ion-density along the track of an α-particle is about 8·9 times greater than that for a β-particle of equal speed. This accounts for the relative distinctness of the tracks as seen in cloud-chamber photographs. It is noteworthy, however, that the calculated energy loss necessary to produce an ion-pair (e.g. for air) is about the same in both cases (approximately 30 volts per ion-pair (A. Becker, 1926)).

15. Scattering of α-rays

Experiments on the Scattering of α-rays.—In passing through matter, α-particles are to some extent deflected from their straight paths, just as light is scattered in passing through a turbid medium. Owing to the relatively large mass and energy of the α-particles, however, the deflections are extremely small as compared with those of electrons. This is seen clearly if we compare α-ray and electron cloud-tracks (see, e.g., fig. 21, p. 39, and fig. 68, p. 79). Even for relatively thick layers of matter the spreading of an initially narrow beam of α-rays amounts to only a few degrees. The phenomenon was discovered in 1906 by RUTHERFORD, who allowed a beam of α-rays to fall upon a photographic plate after passing through a narrow slit. When the whole apparatus was evacuated, a sharp image of the slit was obtained. Admission of air or interposition of a thin foil on the same side of the slit as the photographic plate caused a broadening of the image, the intensity falling off gradually on either side. An extremely important observation was made by GEIGER and MARSDEN in 1909, by using the scintillation method (p. 16). This method has the advantage of permitting the observation of effects due to single α-particles, and so makes it possible to investigate atomic processes occurring so infrequently that they cannot be observed by the photographic method. GEIGER and MARSDEN found that a few of the α-particles incident upon a foil are so strongly deflected that they are thrown back and pass out again on the *same side* of the foil. This effect, known as **large-angle scattering,** resembles the back-scattering of electrons. A quantitative investigation showed that the number of α-particles scattered through large angles increases up to a constant value as the foil thickness is increased and that it also increases very rapidly with the atomic weight of the material used. For platinum the mean number of α-particles scattered through 90° is found to be 1 in 8000. Now this proportion is far greater than one would expect from the results for scattering at small angles mentioned above (which were confirmed by Geiger using the scintillation method). These small-angle deflections are due to the extended fields of force of the atoms concerned, just as we saw was the case for electrons. The anomalously high proportion of large-angle scattering with α-particles indicates that some new process is taking place here, whereby certain of the α-particles have their directions suddenly turned through very large angles. In view of the great energy and mass of the α-particles, it is clear that extremely strong fields of force must come into play in large-angle scattering as compared with small-angle scattering. These considerations led RUTHERFORD (1911) to put forward the theory that *the positively charged part of an atom is confined to a region* (*the so-called* **nucleus**) *which is very small in comparison with the gas-kinetic size of the atom* (*about* 10^{-8} *cm.*), *whereas the electrons of the atom are situated at distances from the nucleus comparable with the size of the atom.* Thus we have to imagine the atom as built up of a very small positively-charged nucleus, surrounded by a system of negative electrons. This atomic model explains small-angle scattering of α-particles as due to deflections caused by the electrons at relatively large distances from the nucleus, while large-angle scattering is explained as due to the deflections which occur when α-particles happen to pass very near the atomic nuclei.

If we regard the sudden change of direction in large-angle scattering as due to Coulomb repulsive forces, then it follows either that the charges involved must be very great or that they must approach each other very closely.

Now experiments on the scattering of electrons and X-rays show that the number of elementary charges involved is at most of the order of magnitude of the atomic weight (pp. 63 and 92). Hence we deduce that these charges must be packed into a very small space in the nucleus; for only at very small distances can Coulomb forces of the requisite magnitude occur. This deduction can be tested in a quantitative manner (see below), and direct photographs of α-ray tracks show that individual "collisions" of α-particles with atomic nuclei do actually take place. (See figs. 74, 75, 76, pp. 90, 91). As the large-angle scattering of α-particles is of such fundamental importance in the theory of atomic structure, we shall now discuss the quantitative deductions.

Collision of α-particles with Nuclei, the Inverse Square Law of Force being assumed.—Let $2e$, m, and v be the charge, the mass, and the velocity of an α-particle approaching a nucleus K (fig. 70) along the line QN. Let the charge of the nucleus be Ze, and let us assume that both nucleus and α-particle may be regarded as points. Since the large-angle deflection of the α-particle (i.e the "collision") occurs at distances which are small relative to the radius of the atom as a whole (see below), the influence of the negative electrons surrounding the nucleus may be neglected. If the inverse square law of force is assumed, the path of the α-particle will be a hyperbola with the nucleus K as focus. Let the angle through which the direction of motion of the α-particle is turned be ϕ. This is the angle between the asymptotes of the hyperbola (see figure). If u is the velocity of the particle at the point P, p the length of the perpendicular KN from K to the initial direction QN, and d the distance KP, then applying the theorem of equal areas (Vol. I, p. 51) to the hyperbola, we have

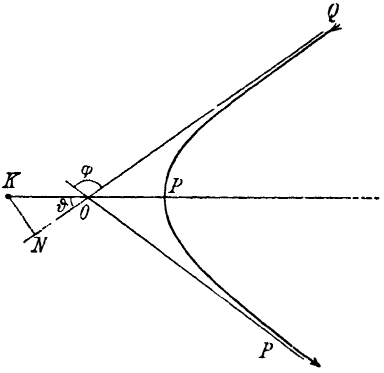

Fig. 70.—Deflection of an α-particle on collision with an atomic nucleus

$$pv = au.$$

By the principle of the conservation of energy,

$$\tfrac{1}{2}mu^2 = \tfrac{1}{2}mv^2 - \frac{Ze \times 2e}{d},$$

the second term on the right-hand side being the potential energy at the point P. Hence, introducing the abbreviation $b = 2Ze^2/(\tfrac{1}{2}mv^2)$, we obtain

$$u^2 = v^2\left(1 - \frac{b}{d}\right).$$

From this equation it is clear that b is the least distance of possible approach for the initial velocity v. (This nearest approach is realized in the case of direct " head-on collision ", when $p = 0$ and the particle is made to return along its own path.)

From the geometry of the hyperbola it follows further that OP is the real semi-axis and that

$$d = \mathrm{KO} + \mathrm{OP} = p \operatorname{cosec}\theta + p \cot\theta = p \cot\frac{\theta}{2}.$$

Again, from the equation expressing the theorem of areas and the equation containing b above (eliminating u^2/v^2), we have

$$p^2 = d(d - b).$$

Hence

$$b = 2p \cot\theta.$$

Now $\phi = \pi - 2\theta$; hence

$$\cot\frac{\phi}{2} = \frac{2p}{b}$$

and

$$d = \frac{b(1 + \sin\frac{1}{2}\phi)}{2\sin\frac{1}{2}\phi}.$$

Example.—If an α-particle from RaC with the velocity $v = 1 \cdot 92 \times 10^9$ cm./sec. collides with a nucleus of charge 100 e, we obtain $b = 3 \cdot 7 \times 10^{-12}$ cm. This, therefore, is an upper limit for the radius of the nucleus, since the actual radius must be less than b.

In the experimental investigation a beam of α-rays is allowed to fall normally upon a foil of thickness t, and the number of α-particles scattered through a definite angle ϕ is observed.

The mean free path of a particle (assumed to be a point) incident upon an assembly of spheres of radius R is

$$\lambda = \frac{1}{\pi \mathrm{R}^2 n}$$

(see Vol. II, p. 49), where n is the number of spheres per cubic centimetre. Hence the number of collisions in passsing through a thickness of t cm. will be $z = \pi R^2 nt$. In the same way the number of nuclei passed at a distance p is $z' = \pi p^2 nt$. The number passed at distances between p and $(p + dp)$ is therefore $dz' = 2\pi pnt\,dp$, or, in terms of b and ϕ, $\frac{1}{4}\pi ntb^2 \cot\frac{1}{2}\phi \operatorname{cosec}^2\frac{1}{2}\phi\,d\phi$. This is the fraction of α-particles which suffer deflections between the angles ϕ and $(\phi + d\phi)$.

In the actual experiments a zinc sulphide screen, placed at a distance r from the scattering foil, is observed through a microscope, and the number of scintillations over the constant area defined by the field of view is counted. The screen is placed in different positions corresponding to different angles ϕ. If Q is the total number of particles and dz' the fraction scattered in the direction corresponding to values of p between p and $(p + dp)$, the fraction observed per unit area of the screen will be

$$y = \frac{Q\,dz'}{2\pi r^2 \sin\phi\,d\phi}.$$

Substitution of the value obtained above for dz' gives

$$y = \frac{ntb^2 \operatorname{cosec}^4 \frac{1}{2}\phi}{16r^2},$$

where

$$b = 2Ze^2/(\tfrac{1}{2}mv^2).$$

If the above discussion is correct, it follows that the number of scintillations must be (*a*) directly proportional to $\operatorname{cosec}^4\frac{1}{2}\phi$; (*b*) directly proportional to t (this applies only to thin foils, as otherwise multiple scattering occurs); (*c*) directly proportional to Z^2; and (*d*) inversely proportional to v^4.

Experimental Results.—The scattering of α-particles was investigated in detail by GEIGER (1911) and GEIGER and MARSDEN (1913).

(*a*) Fig. 71 shows the very simple apparatus for determining the variation with angle. This consists of a lower part C in which a tube T is rigidly mounted. Fixed to this tube is the holder containing the radioactive preparation R (a small tube containing radium emanation). The α-rays pass through an aperture D in the form of a narrow sharply-defined beam and fall upon the foil F, which is also rigidly attached to the tube. In the upper part of the apparatus there is a ground joint with a base plate A and a metal box B closed above by a glass plate P. At the side is the microscope M, with the phosphorescent screen S fixed rigidly to it at the correct distance from the objective. The base plate, together with the box and microscope, can be rotated in the ground joint so as to enable observations to be made for different ranges of angle. The whole is hermetically sealed and evacuated through the tube T, so as to avoid scattering due to the air.

Gold and silver foils were investigated, the angle was varied between 150° and 5°, and two different radioactive preparations were used. The experiments showed that *the number of scattered particles is proportional to* $\operatorname{cosec}^4 \frac{1}{2}\phi$ (see above).

(*b*) The apparatus used to investigate the variation of scattering with the thickness and the nature of the scattering substance is shown in fig. 72. The round brass box A is closed on both sides by glass plates. The α-rays from the radioactive substance (RaC) in R enter through a thin mica window E. The foils of various thicknesses and substances are carried by the round disc S, which can be rotated by means of the ground joint M so as to bring them successively into the path of the beam passing through D. The fixed phosphorescent screen is shown at Z. It is observed from outside by the microscope.

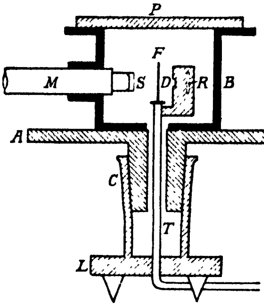

Fig. 71.—Geiger and Marsden's apparatus for measuring the scattering of α-particles.

[From *Handbuch der Physik*, Vol. XXII (Springer, Berlin).]

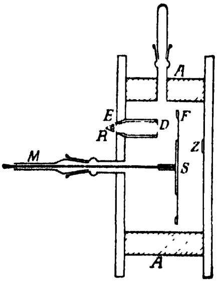

Fig. 72.—Geiger and Marsden's apparatus for measuring the effect of the thickness of the foil.

[From *Handbuch der Physik*, Vol. XXII (Springer, Berlin).]

Actual counting experiments showed that *for thin foils the number of scattered particles is proportional to the thickness* (see above).

(*c*) Comparison of the scattering produced by different metals (e.g. Au, Pt, Sn, Ag, Cu, Al) gave the result that, when reduced to equal numbers of atoms per unit volume, *the scattering is approximately proportional to the square of the atomic weight.* This indicates that the nuclear charge Z is approximately proportional to the atomic weight.

(*d*) In order to investigate the variation of the scattering with the velocity of the particles, different thicknesses of mica were interposed between R and E so as to produce different reductions of velocity. The experiments showed that *the number of particles scattered through a given large angle is inversely proportional to the fourth power of the velocity.*

Thus detailed experimental investigation proves not only that (as can be seen directly from cloud-track photographs) the scattering is due to single encounters, but also that Coulomb's inverse square law of force holds good down to distances of the order of 10^{-11} cm., and that the positive charges of the nucleus must be packed into a region with a radius even less than this.

16. The Nuclear Charge and the Nuclear Field

Experimental Determination of the Nuclear Charge.—MOSELEY'S investigations (p. 75) show that the *atomic numbers*, and not the atomic weights, determine the electrical behaviour of atoms. The results given above for α-ray scattering provide a basis for the determination of nuclear charges by the absolute measurement of the number of incident α-particles and the number scattered under definite conditions. Such determinations were carried out by CHADWICK in 1920, using the scintillation method. He obtained the following values: Pt, 77·4; Ag, 46·3; Cu, 29·3. Now the corresponding atomic numbers are 78, 47, and 29. This is direct quantitative proof of the following important result:

The atomic number is equal to the net positive charge of the nucleus expressed in elementary units and hence is equal to the number of electrons surrounding the nucleus.

Scattering of α-particles by Light Elements.—The distribution of the numbers of α-particles scattered at different angles forms a very sensitive criterion of the validity of the inverse square law assumed in the above discussion. CHADWICK and RUTHERFORD and also ROSE made experiments with α-particles of different speeds and found that over the range investigated the inverse square law holds within an accuracy of a few per cent. This is true for platinum and gold at distances from $3{\cdot}2 \times 10^{-12}$ up to $1{\cdot}7 \times 10^{-10}$ cm. from the nucleus, for silver down to 2×10^{-12} cm. and for copper down to $1{\cdot}2 \times 10^{-12}$ cm.

From this it follows that the actual *nuclei* of the elements must be *very much smaller still*; for they doubtless contain a complex assemblage of positive and negative charges (p. 105), so that the very close approach of a charged particle might be expected to produce polarization effects and consequent deviations from the inverse square law. Such deviations have actually been observed in the case of the lighter elements. The nuclear charges being here smaller, the repulsive forces are also smaller, and α-particles of sufficient velocity are able to approach correspondingly nearer to the nuclei—in some instances even penetrating right into them. Where penetration occurs, energy may be given up to the interior of the nucleus and the collision is then inelastic (p. 90). Moreover, in the mathematical treatment of the collision of an α-particle with a light nucleus, it is no longer permissible to make the simplifying assumption that the nucleus remains at rest. The recoil of the nucleus, which becomes appreciable as the atomic weight decreases (for aluminium it amounts to 4 per cent), can easily be taken into account in the calculation.

Deviations from the inverse square law were observed for aluminium and magnesium by BIELER (1924) and by RUTHERFORD and

CHADWICK (1925). Since, however, the impact of fast α-particles upon the nuclei of these elements may produce other (though probably rarely-occurring) phenomena which affect the scattering (p. 105), there is some uncertainty about the meaning of these results. There is no doubt, however, that the scattering is less than that which would be expected on the basis of the inverse square law, and the limiting distance of approach at which the law is still valid is probably about $1{\cdot}2 \times 10^{-12}$ cm.; it certainly does *not* hold for distances less than about 8×10^{-13} cm.

The circumstances are clearer for collisions with helium and hydrogen nuclei. Since the mass of the hydrogen nucleus is only a quarter that of the α-particle, the velocity imparted to the former by a "head-on" collision is greater than that of the α-particle—actually 8/5 of the latter (see below). This means, for example, that an α-particle from RaC′ must impart to the hydrogen nucleus which it strikes a velocity sufficiently great to give it a range of 30 cm. in air or 120 cm. in hydrogen. Such long-range H-particles were first observed by MARSDEN in 1914 and investigated in detail by RUTHERFORD in 1919. The measured range was over 100 cm. in hydrogen and 28 cm. in air. That the particles really were hydrogen nuclei was proved by electric and magnetic determination of e/m, and also (1925) by STETTER, who used a mass spectrograph (p. 99).

Counts of the H-particles showed that when very swift α-particles were used their number was very much greater than that expected on the basis of the law of inverse squares (up to 100 times as great), but that the agreement improved as the velocity of the α-particles was decreased, i.e. as their distance of nearest approach to the nuclei was increased. The experimentally-observed angular distribution of deviations (CHADWICK and BIELER, 1921) leads to the following result. For direct head-on collisions the inverse square law holds down to a distance of about 4×10^{-13} cm.; for oblique collisions down to about 8×10^{-13} cm. From this it has been concluded that the α-particle must be disc-shaped, at least in the strong field during the collision.

The investigations of scattering by helium nuclei (RUTHERFORD and CHADWICK, 1927) gave essentially similar results. Here too there are strong indications that the field distribution deviates (at least during collision) from the spherically-symmetrical. For head-on collisions the inverse square law is found to hold down to about $3{\cdot}5 \times 10^{-13}$ cm.; for oblique collisions only down to $1{\cdot}4 \times 10^{-12}$ cm.

Laws of the Conservation of Energy and Momentum during Collision.—These laws must necessarily be true for the kinetic energies and momenta of particles before and after an elastic collision, quite independently of the particular law of force. Deviations may well occur, however, if energy is taken up by either particle and stored within it as internal energy; such deviations indicate that energy transformations are taking place.

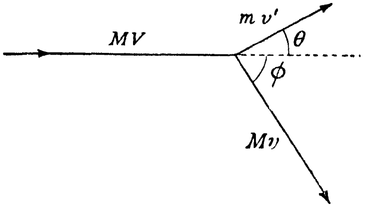

Fig. 73.—Diagram of collision

Using the symbols shown in fig. 73, in the case of elastic collision we have the following equations:

(1) For the momenta in and at right angles to the direction of collision:

$$\mathrm{MV} = \mathrm{M}v\cos\phi + mv'\cos\theta,$$
$$0 = \mathrm{M}v\sin\phi - mv'\sin\theta.$$

(2) For the energies:

$$\mathrm{MV}^2 = \mathrm{M}v^2 + mv'^2.$$

Hence

$$v' = 2\mathrm{V}\frac{\mathrm{M}}{\mathrm{M}+m}\cos\theta;\quad \tan\phi = \frac{m\sin 2\theta}{\mathrm{M}-m\cos 2\theta};$$

$$v = \frac{\mathrm{V}}{\mathrm{M}+m}[\mathrm{M}\cos\phi \pm \sqrt{m^2-\mathrm{M}^2\sin^2\phi};$$

$$\tan\theta = \frac{m\cot\phi \pm \sqrt{m^2\operatorname{cosec}^2\phi - \mathrm{M}^2}}{\mathrm{M}+m}.$$

For direct head-on collision ($\phi = \theta = 0$) the velocity imparted to the struck nucleus by an α-particle of original velocity V is therefore 1·6 V for H, V for He, ½V for C, and 0·4 V for O. In actual practice the velocities after collision can be calculated from the observed ranges in the cases of He and H (e.g. for α-particles by the GEIGER relationship, p. 80). For other atoms, however, this is not directly possible, because we do not know how many extra-nuclear electrons the atom loses at these velocities. The α-particles scattered through different angles ϕ have different ranges, since v depends upon ϕ.

The experimental results of measurements with different substances are in good agreement with the formulæ given above. This is evidence for the assumption that laws of conservation of energy and momentum hold in these collisions.

Stereoscopic cloud-track photographs offer particularly clear evidence on this point. The angles concerned can be computed directly from the photographs, which also show the ranges. Fig. 74 shows a pair of stereoscopic photographs in which a collision of an α-particle with a hydrogen nucleus is visible. In fig. 75 the collision is between an α-particle and a helium nucleus, the angle between the tracks after the collision being a right angle and the lengths of the tracks equal.

Fig. 76 shows the collision of an α-particle with an oxygen nucleus, which here gives rise to the shorter limb of the fork. When the necessary measurements are made, these examples are found to agree with predictions based on the laws of conservation of energy and momentum.

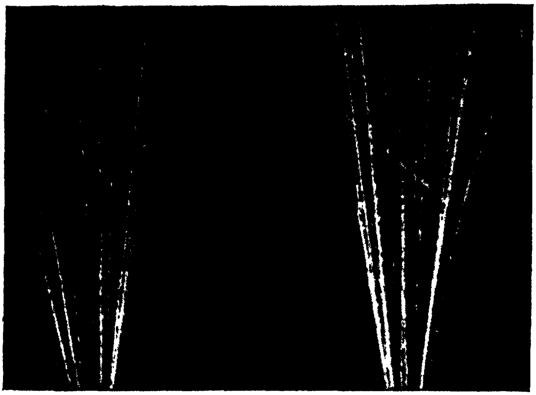

Fig. 74.—Collision of an α-particle with a hydrogen nucleus (stereoscopic cloud-chamber photograph)

[From Rutherford, Chadwick, and Ellis, *Radiations rom Radioactive Substances.*]

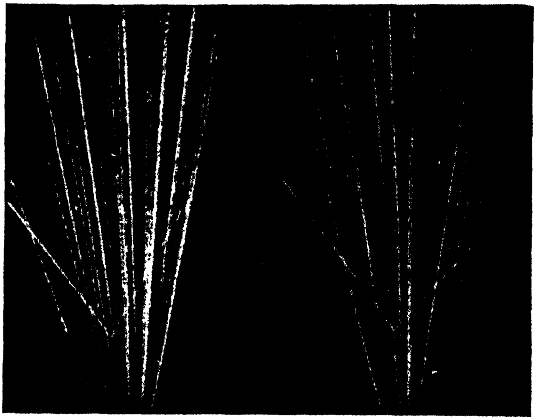

Fig. 75.—Collision of an α-particle with a helium nucleus

[From Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances.*]

In some cases, however, the observed kinetic energies are not in agreement with these laws (Auger and Perrin, 1922). This indicates that in certain circumstances energy may be imparted to the struck

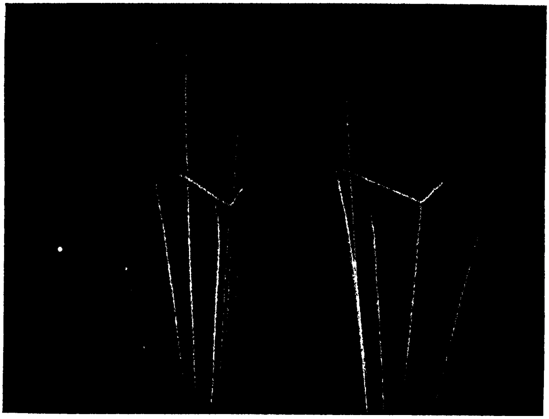

Fig. 76.—Collision of an α-particle with an oxygen nucleus

[From Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances.*]

nucleus and stored within it as internal energy. (See further p. 87.) In some cases this energy may be given up again by the nucleus in the form of electromagnetic radiation (γ-rays).

F. ATOMIC STRUCTURE

17. Summary of the Experimental Results

At this point it will be useful to give a summary of the conclusions as to atomic structure which can be drawn from the facts hitherto described.

Charge Distribution.—Every atom consists of an assemblage of positive and negative charges, the distribution being such that the positive charges (and with them the material mass of the atom) are concentrated at the centre. The effective diameter of this positive region, the so-called **nucleus,** has been found to be 10^{-13} to 10^{-12} cm. The nucleus is surrounded by a number of negative electrons sufficient to make the whole atom electrically neutral. The maximum distance of these **extra-nuclear electrons** from the nucleus is about 10^{-8} cm. in the normal state of the atom. Their fields may be effective at much greater distances, as is shown by investigations of the diffusion of slow electrons (p. 44). Table X gives a list of effective atomic radii, i.e. the distances at which the forces become so strong as to prevent the closer approach of other atoms in collisions at velocities of the order of those of the thermal motion at room temperature. Such values can be derived from various considerations (gas-kinetic radii, Vol. II, p. 50). An upper limit is also obtained from the specific volumes of solids or liquids. Since the theory of melting makes it probable that

TABLE X.—DIAMETERS OF CERTAIN ATOMS IN ÅNGSTRÖM UNITS (1 Å. = 10^{-8} cm.)

C	1·40	Si	2·06	Ca	3·47	Ag	2·57
Na	3·23	A	3·51	Fe	2·30	Au	2·58
Al	2·59	K	3·82	Cu	2·27	Pb	3·12

at the melting-point the distance between the atoms of a solid is only about 10 per cent greater than the atomic diameter, the atomic volume (i.e. the volume of a gramme-atom, which contains the same number of atoms in all cases) forms a good measure of the relative size of atoms. The different possible arrangements of the atoms or molecules in a lattice are of secondary importance here. A graphical representation of the atomic diameters of the elements as a function of the atomic numbers has already been given in fig. 1 (p. 7). A discussion of this curve follows on p. 299.

Non-Periodic and Periodic Properties.—LENARD (p. 33) was the first to show by a study of the absorption of cathode rays that the electromagnetic fields of atoms increase in intensity in rough proportion to the atomic weight. In this respect, therefore, there is no parallel to the manifold individual differences exhibited by the different elements in their other properties. It has further been shown above that if the elements are arranged in the order of increasing atomic weight, there is (in all but a few exceptional cases) a regular increase of the nuclear charge by one elementary unit ($e = 1{\cdot}59 \times 10^{-19}$ coulombs) and a corresponding increase of one in the number of extra-nuclear electrons as we pass from any element to the next in the series. Thus every element has its own **atomic number** Z, equal to the number of elementary units in the net nuclear charge and also to the number of electrons surrounding the nucleus in the neutral atom. MOSELEY'S results (p. 76) show that arrangement of the elements in the order of increasing atomic diameters corresponds to the character of their X-ray spectra (p. 75), while the same order is found to underlie the phenomena of the absorption of X-rays (p. 60).

The identity of this order with the order of increasing nuclear charge is most clearly seen from the experiments of CHADWICK (p. 87), in conjunction with the result obtained from X-ray scattering that in light elements the number of electrons per atom is equal to half the atomic weight (p. 63).

In fig. 77 atomic weights are shown plotted against atomic numbers (the dotted curve). The curve starts for low atomic numbers as a straight line inclined to the horizontal at an angle which indicates that each increase of the nuclear charge by one unit is accompanied by an increase of the atomic weight by two. As we pass to the higher atomic numbers (heavier atoms), however, the curve deviates from the straight line, the increase of atomic weight becoming more rapid. We have seen (p. 26) from the existence of isotopes (elements of the same atomic number but different atomic weight) and isobares (elements of the same atomic weight but different atomic number) in radioactive changes, that the atomic weight is not the quantity that determines the chemical properties. This quantity is in fact the atomic number (see the displacement law of FAJANS and SODDY (p. 26)). Another important fact is the great difference between the chemical properties of a neutral atom and those of the corresponding ion. This shows that it is not the mass of the nucleus, but the number of extra-nuclear electrons, that determines chemical behaviour.

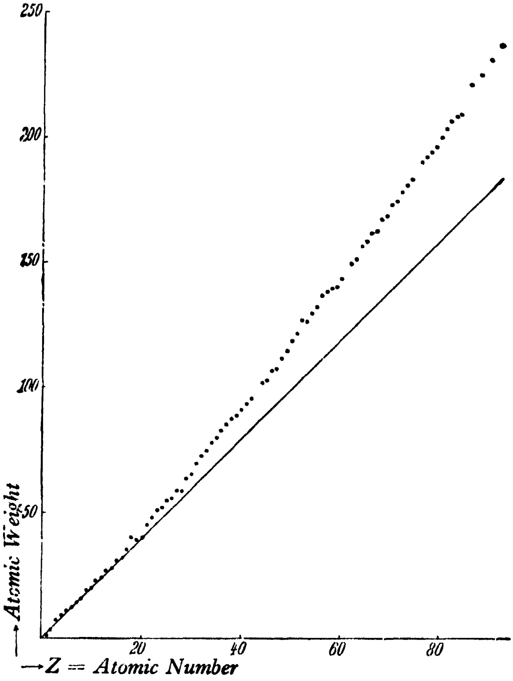

Fig. 77.—Atomic weight plotted against atomic number

From the fact that the atomic weights are not the same as the atomic numbers it follows that atomic nuclei must contain other particles in addition to elementary positive particles (protons). Each proton has unit mass; but for He (atomic number 2) the atomic weight has already risen to 4 units. Hence in addition to two protons the helium nucleus must contain particles equivalent to two neutral hydrogen atoms. Of course these extra particles must be present in some form entirely different from ordinary hydrogen atoms; for the diameter of the region they occupy in the helium nucleus is at least 100,000 times smaller.

The question now arises, how are the positive and neutral particles arranged within the nucleus, and to what conditions are they subject? These questions will be dealt with in the next chapter.

In contrast to the approximately linear dependence of certain properties upon the atomic number mentioned above, we have the well-known wide variation of the elements in many other physical properties and especially in chemical behaviour. Since the pioneer work of MENDELÉEFF (1869) and LOTHAR MEYER (1864) the **periodic** variation of chemical and certain other properties with atomic weight (more accurately, with atomic number) has become increasingly apparent. This is expressed in the periodic table of the elements (Table I, p. 4). Elements with similar properties occur at regular intervals when the elements are arranged in order of increasing atomic number.

Thus, e.g., the elements with the atomic numbers 2, 10 ($=2+8$), 18 ($=2+8+8$), 36 ($=2+8+8+18$), 54 ($=2+8+8+18+18$), and 86 ($=2+8+8+18+18+32$) are all inert gases. Similarly, the elements with atomic numbers one higher than the inert gases (3, 11, 19, 37, 55) belong to the so-called group of the alkali metals, which chemically are very closely related and have a strongly electropositive character (i.e. a strong tendency to lose an electron). Again, the elements with atomic numbers one lower than the inert gases are all closely related chemically and have a strongly electronegative character (i.e. a strong tendency to take up an electron). Thus we have a very striking and regular periodicity based upon the numbers 2, 8, 18, 32. These numbers can be written in the form 2×1^2, 2×2^2, 2×3^2, and 2×4^2. The significance of this will become clear in a later section (p. 333), when the theoretical basis of the periodic table is discussed in greater detail.

A large number of properties other than chemical properties exhibit the same periodicity, a fact which shows that they depend upon the extra-nuclear electronic configuration. The periodic variations in atomic volume, i.e. in the distances between atoms as determined by their fields of force, are represented graphically in fig. 1, p. 7. Melting-points, which are closely connected with atomic volumes, show the same sort of periodicity (see fig. 2, p. 8), and similar variations are also found in coefficients of thermal expansion and in compressibilities. Further examples of the periodicity of atomic properties will be met with later. Particular importance attaches to the periodic variations in the optical spectra, which are quite analogous to the variations in chemical behaviour. The study of these spectral periodicities has supplied a quantitative answer (see p. 336) to one of the most important questions in connexion with atomic structure: what is the relationship between the observed periodic variations of properties and the arrangement of the electrons around the nucleus? Obviously the periodicities indicate that the electronic arrangement must be in some way periodic. A detailed theory was first put forward by BOHR (see p. 343).

CHAPTER II

The Nucleus

1. Isotopy

Nuclear Mass.—The evidence discussed in Chapter I leads to the conclusion that the positively-charged part of an atom, which carries nearly the whole of the mass, is concentrated into a small region, the so-called **nucleus,** with a diameter of about 10^{-12} cm. The magnitude of the nuclear charge determines the chemical character of the atom: every chemical element has its characteristic nuclear charge (p. 87), which when expressed in elementary units is numerically equal to the atomic number. Does the nuclear mass similarly have a characteristic value for each element? The consideration of radioactive substances (p. 25) has shown that this is *not* the case. Different radioactive disintegration series give rise to products which are chemically identical but have different nuclear masses. We have already learned (p. 26) that these chemically inseparable types of atoms are called **isotopes.** Thus the atomic weights of samples of lead from different sources in which it is associated with radioactive elements may vary by several units.*

The discovery of isotopy in connexion with radioactivity raised the question whether the ordinary elements consist of mixtures of isotopes.

It had long before been noted that a large number of elements (namely those with low atomic numbers) have atomic weights which are nearly whole numbers when referred to oxygen as 16·000. As was pointed out as early as 1815 by the English physician PROUT, this would seem to indicate that the masses of all atoms are integral multiples of the mass of a hydrogen atom, which is (approximately) unity. The atomic weights of certain elements (notably chlorine), however, differ quite definitely from whole numbers, and consequently PROUT's hypothesis soon lost favour. The discovery of isotopy opened up the possibility that such elements might consist of mixtures of isotopes, each of integral atomic weight, the average atomic weight having an intermediate non-integral value. Thus, for example, if ordinary chlorine were a mixture of two isotopes of atomic weight 35 and 37 in the proportion 3 : 1, the observed average atomic weight would be 35·5 (the actual value found).

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* On the other hand, the atomic weight of lead (or any other element) derived from sources containing no radioactive elements is *always the same*, whether it is obtained from volcanic material, sedimentary rocks, or even meteorites.

J. J. THOMSON * was the first to prove (1912), by the method described below, that neon consists of a mixture of two isotopes of atomic weight 20 and 22. This was the first non-radioactive element shown to be a mixture of isotopes.

Amongst the radioactive elements we encounter various isotopes either by themselves or in a variety of proportions. In order, however, to obtain the individual isotopes of ordinary stable elements, or at least to obtain mixtures containing new proportions of the isotopes, it is necessary to subject the natural mixture to some treatment in which the difference in the masses of the isotopes plays a part. Three methods have proved specially successful: diffusion through porous partitions (Vol. II, p. 63), evaporation at low temperatures, and evaporation at very low pressures (so-called ideal distillation).

Two fractions of different densities have been obtained from neon (ASTON) and HCl (HARKINS) by the first of these methods, from neon (KEESOM and VAN DIJK) by the second method and from mercury and HCl (BROENSTED and HEVESY) by the third. The mean atomic weights of the two mercury fractions, for example, were respectively 200·63 and 200·56 as compared with 200·61 for ordinary mercury. HARKINS has recently obtained fractions with atomic weights 200·71 and 200·52. In 1932 G. HERTZ greatly improved the diffusion method by applying the counter-current principle. In this way he succeeded in obtaining neon 20 containing only 1 per cent of Ne 22.

The relative mass difference is particularly great in the case of the isotopes of hydrogen, one of which has mass 1 (ordinary hydrogen) and the other mass 2 (so-called *diplogen* or *deuterium*). The proportion of the heavy isotope in the naturally-occurring mixture is about 1 part in 4000. Water containing a high proportion of the heavy isotope (so-called "heavy water") can be obtained relatively easily by electrolysis (WASHBURN). The lighter isotope escapes more readily than the heavier, which is thus concentrated in the residual liquid. "Heavy water" has a higher density than ordinary water. It also has a higher boiling-point, so that the heavier isotope can also be concentrated by distillation.

By the above methods it is possible to concentrate different isotopes, but never to achieve absolutely complete separation. In this respect the method described in the next section is a more powerful one.

2. Detection of Isotopes

J. J. Thomson's Parabola Method.—Consider a beam of canal rays (positive rays) passing through a region containing an electric field with the lines of force at right angles to the beam and at the same time a magnetic field with its lines of force in the same direction as those of the electric field and in the same or the opposite sense. The positive particles will then be deflected in such a way that the trace produced on a plate normal to the beam is a parabola (for proof, see below). This is illustrated in fig. 1. The beam of positive particles is normal to the plane of the figure and is directed away from the observer towards the point O. It passes between two plates, one of which (say the left one) is maintained at a constant positive potential relative to the other. Then the electric lines of force will run from left to right in the figure. A magnetic field is also maintained in the space between the plates, such that the magnetic lines of force also run from left to right. The electric field displaces the positive particles to the right by an amount which may be calculated as in Vol. III, p. 314, while the magnetic field displaces them downwards in the figure (Vol. III, p. 316). If we use the co-ordinates shown in the figure, these displacements are given by

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* Sir J. J. THOMSON (1856–1940) became Lecturer in Physics at Trinity College, Cambridge, in 1883; then from 1884 to 1918 held the position of Cavendish Professor of Physics at Cambridge, and also that of Professor of Physics at the Royal Institution, London. He was knighted in 1908, and in 1918 became Master of Trinity College, Cambridge. At Cambridge he carried out fundamental researches on the conduction of electricity through gases, the charge and mass of the electron, positive ray analysis, &c.

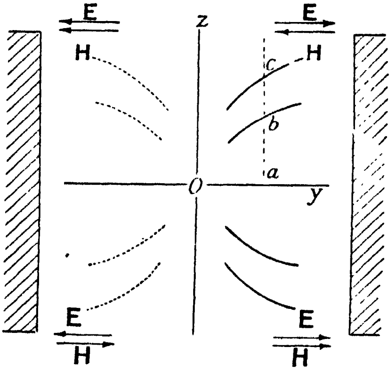

Fig. 1.—Parabolic traces of positive rays deflected by parallel electric and magnetic fields.

$$y = \tfrac{1}{2}a^2 \frac{eE}{mv^2}; \quad z = \tfrac{1}{2}b^2 \frac{eH}{mv},$$

where a and b are the distances passed through in the electric field of strength E and the magnetic field of strength H respectively, and e, m, and v have their usual meanings.

After passing through a field-free region the positive rays fall on a photographic plate. The displacements y' and z' on the plate are proportional to

$$\frac{e}{m}\frac{E}{v^2} \quad \text{and} \quad \frac{e}{m}\frac{H}{v}$$

respectively. Eliminating v, we obtain

$$y' = C\frac{E}{H^2}\frac{m}{e}z'^2.$$

Thus for particles with different velocities but the same value of e/m we obtain a parabola, the shape of which depends upon m/e, the field strengths used, and the dimensions of the apparatus. Each value of m/e thus gives a different parabola, the other factors remaining constant. The point O in fig. 1 is the point at which the beam would strike the plate if there were no fields present, or the point of incidence of particles of infinite velocity if the fields were switched on. Since no particle can possess a velocity greater than that corresponding to the accelerating potential, the parabolas do not extend right up to the point O. The value of y' for a given value of z' increases with m/e, so that the parabolas nearer the y-axis correspond to the particles of greater mass or lesser charge. The ratio of two different masses bearing the same charge is obtained at once by measuring the distances *ab* and *ac* (see fig. 1). From the relations given above we have $m_1/m_2 = ab^2/ac^2$, independently of the dimensions of the apparatus and the conditions of the experiment. The four similar sets of parabolic arcs in fig. 1 correspond to the combinations of field directions indicated in the respective quadrants. Fig. 2 shows parabolas actually obtained with positive rays from neon. In addition to parabolas for the two neon isotopes 20 and 22, traces due to various carbon compounds (from grease vapour) and mercury (from the pump) can be seen. Fig. 3 shows parabolas for certain compounds of carbon and hydrogen.

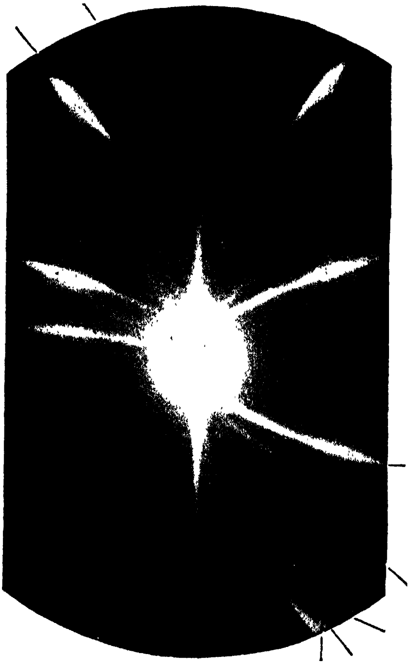

Fig. 2.—Positive ray parabolas with discharge tube containing neon
[From F. W. Aston, *Isotopes* (Arnold).]

Aston's Method.—The method of Thomson was greatly improved by Aston * (1919). He used crossed fields and developed an apparatus (the so-called **mass spectrograph**) with which atomic weights could be determined to within 0·01 per cent.

The apparatus is shown diagrammatically in fig. 4.

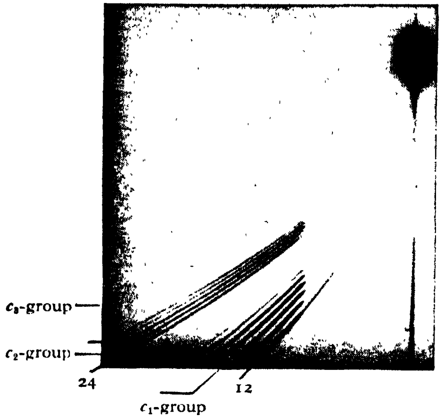

Fig. 3.—Positive ray parabolas for hydrocarbons

[After Eisenhut and Conrad, *Zeitschrift fur Elektrochemie*, Vol. XXXVI (1930).]

The discharge is produced in the spherical globe B, A being the anode and C the cathode. The latter, as in W. Wien's apparatus (Vol. III, p. 342), has a very fine channel S_1 (0·03 mm. wide) running through it. The positive rays pass through this tube before entering the observation space on the left. They are further restricted so as to form a narrow beam by means of a second slit S_2, which is accurately centred with the first. They then pass between the plates

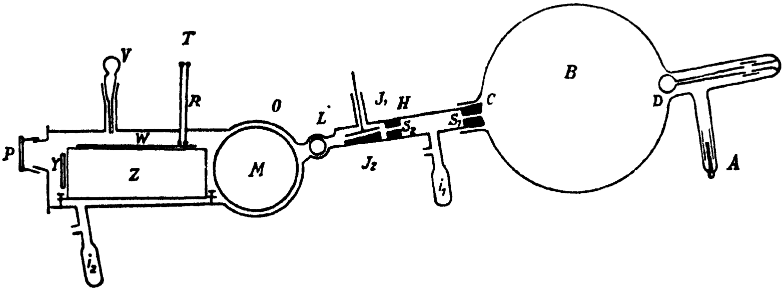

Fig. 4.—Aston's mass spectrograph

J_1, J_2, between which an electric field is maintained, as in a condenser. The field deflects the beam and at the same time resolves it into a " spectrum " of rays of different energies (velocities). Another slit L, situated in the bore of a ground tap, can be finely adjusted so as to let through a smaller or larger angular region of the dispersed beam. Thus the particles passing through L have kinetic energies included in a certain small range. They next pass between the poles M of a very powerful electromagnet, the lines of force from which are at right angles to the lines of force of the electric field. The magnetic field strength is adjusted in such a way that the deflection produced by it is just twice that produced by the electric field and in the opposite direction. This being so, the rays dispersed by the electric field are focussed by the magnetic field and form a sharp " image " of the slit. For suppose that the rays passing through L are deflected through an angle φ by the electric field, and through an angle ψ by the magnetic field. The magnitude of φ is given by $e/(v^2m)$; that of ψ by $e/(vm)$ (see above, p. 97). The velocity v in general varies considerably, but for a given m only particles with velocities lying in the small range Δv get through L. The corresponding small angular dispersion, which we may call $\Delta\varphi$, is given by $2e\Delta v/(v^3m)$. Since the velocities are spread out over the small region Δv, the magnetic deflections will also be spread over a small angular region $\Delta\psi$, which is given by $e\Delta v/(v^2m)$. Hence we have

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* F. W. Aston, born in 1877, became assistant lecturer in Physics at Birmingham University in 1909, and went to Trinity College and the Cavendish Laboratory, Cambridge, in 1910. In 1922 he was awarded the Nobel Prize for his work on isotopes.

$$\frac{\Delta\psi}{\psi} = \frac{\Delta\varphi}{2\varphi}.$$

Now if we adjust the magnetic field strength so that $\psi = 2\varphi$, it follows that $\Delta\psi = \Delta\varphi$. Since, further, the magnetic and electric effects oppose one another, the dispersion is just neutralized. The divergent beam passing through L is thus brought to a definite focus for each value of m by the magnetic field. In this respect the magnetic field does for the canal rays what a converging lens does for a beam of light from a point source. The extreme sharpness and accuracy of Aston's method depends upon this focussing property.

After deflection by the magnetic field the beam enters a photographic camera Z and falls in focus on the plate W. The side-tubes I_1 and I_2, which contain coconut carbon and dip into liquid air, absorb residual gases and thus maintain a very high vacuum throughout the whole space from the camera to the rear side of the cathode, so preventing any serious broadening of the beam and alterations of velocity as a result of collisions with gas molecules.

The heating effect of the cathode rays from C is made innocuous and the production of X-rays is avoided by the use of the silica bulb D. The light source T and the tube R are used to make reference marks on the photographic plate W (the small dots to the left in fig. 5, p. 101). The correct adjustment of the deflection by regulation of the fields is carried out with the help of the phosphorescent (willemite) screen Y. P is a detachable transparent cover, through which new photographic plates are introduced. Finally, V is a mechanism for shifting the photographic plate after each exposure, so as to bring it into position for the next.

Different positive-ray traces are obtained on the photographic plate according to the nature of the gas in the discharge tube B. Since the slit L selects a narrow range of velocities for each mass from the electrostatic positive-ray spectrum, and since the dispersion is just neutralized by the magnetic field, the final deflection depends on the value of e/m and the strength of the magnetic field only (p. 97), the effect of velocity being eliminated. Thus the positions of the different marks on the plate correspond to different values of e/m.

Mass Spectra.—Fig. 5 shows a series of photographs for the gases neon, chlorine, argon, krypton, and xenon. From their similarity to photographs of optical spectra, Aston called such photographs *mass* *spectra.* Thus each " spectral line " corresponds to a definite ratio of mass to charge.

If we assume that every particle carries just one elementary charge, the smaller the mass of the particle, the greater is the deflection, and hence the closer do the corresponding lines lie to the reference dot at the left-hand end of the spectra. It is possible to mark on the spectrum a calculated *scale of atomic weights* and then to read off from this scale the atomic weight corresponding to any line.

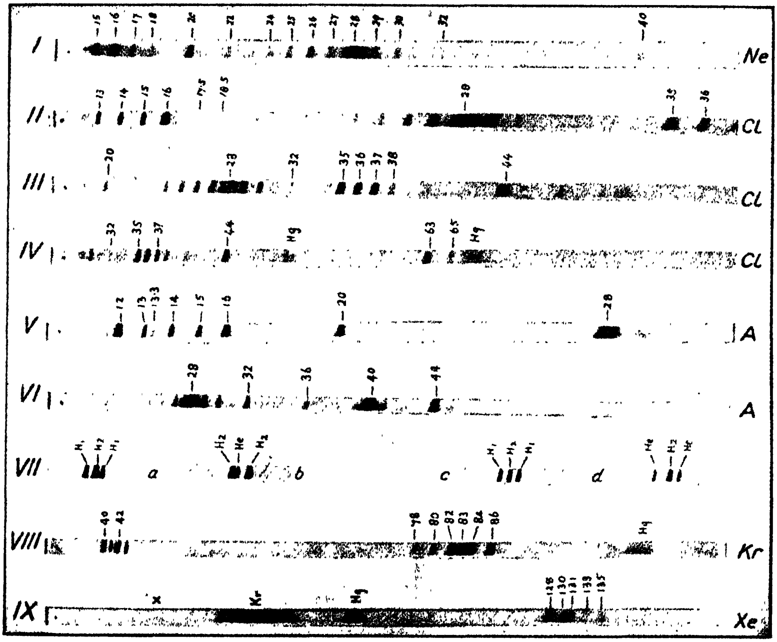

Fig. 5.—Mass spectra

If a particle carries two elementary positive charges, its deflection will be just twice as great as if it carried only one. Hence the line produced in the mass spectrum will be at a point on the scale corresponding to an atomic weight exactly half the correct value. By analogy with grating spectra, ASTON called such lines *lines of second order.* A triply charged particle gives a *line of third order.* Thus an oxygen atom carrying one positive charge gives a line at the scale-value 16, while a doubly charged oxygen atom gives a line at 8. An aluminium atom with one positive charge gives a line at 27, with two charges it gives a line at 13·5, with three charges a line at 9.

Reference Lines.—Certain lines are found on all photographs of mass spectra: these arise from the gases present as impurities in the discharge tube. Chief among such gases are the vapours from tap grease: CO_2 with molecular weight 44, CO and C_2H_4 (ethylene) with molecular weight 28. Singly charged molecules of these gases give lines, which may be used as reference marks, at the corresponding scale values. In addition we have $O_2^+ = 32$, $O^+ = 16$, and $O^{++} = 8$. The mass numbers of unknown lines can be obtained by interpolation between these known values.

The accuracy is even high enough to distinguish between $He^{++} = 2{\cdot}0005$ and $H_2^+ = 2{\cdot}016$ (fig. 5, spectrum VII, *b*). All the four spectra marked VII in fig. 5 were taken with the object of investigating whether the ratio of the atomic weights of helium and hydrogen is a whole number within the limits of accuracy of the method. If the ratio were a whole number, then the line of $He^+ = 4$ taken with a certain field strength must coincide exactly with the line of $H_2^+ = 2$ taken with a field strength just half as great. The test becomes even more delicate if, as in the spectra VII of fig. 5, the first field strength is not exactly twice the second, but a few volts higher or lower than this. If the atomic weights are in the exact ratio 2 : 1, the line of the higher mass must then lie exactly midway between the lines of the lower mass (VII, *a* and *c*). Otherwise the arrangement must be asymmetrical (VII, *b* and *d*).

The Whole-number Rule.—Investigations of mass spectra lead to the following new and surprising result:

The atomic weights of all atoms referred to oxygen as 16·000 *are very nearly whole numbers.*

We may illustrate this result by the case of chlorine. Careful chemical determinations of the atomic weight of ordinary chlorine give the value 35·46. Yet there is no trace of a line in the mass spectrum at the position corresponding to this value (fig. 5, III and IV). Instead, with chlorine or chlorine compounds ($COCl_2$) in the discharge space, we obtain four sharp lines at positions corresponding to 35, 36, 37, and 38 on the atomic weight scale. Not all the four lines recur, however, in the second order spectrum. If each of the four lines in the first order were due to singly charged atoms, we should expect the same atoms when doubly charged to give four lines at $35/2 = 17{\cdot}5$, $36/2 = 18$, $37/2 = 18{\cdot}5$, and $38/2 = 19$. As is stated above, however, this is not the case. Actually only the lines 17·5 and 18·5 occur in the spectra (fig. 5, II).* Hence the lines 36 and 38 must be due to HCl molecules, which (in accordance with the results of THOMSON's canal ray investigations) do not occur with more than one charge (p. 96). Only the lines 35 and 37 remain for chlorine itself. This is confirmed by the fact that when the discharge tube is filled with $COCl_2$ only two lines are found (at 63 and 65) instead of a single line corresponding to the ordinary molecular weight of COCl (63·46) (see fig. 5, IV). The result of investigations of mass spectra is thus as follows:

The ordinary chemical element chlorine is not a simple element consisting of atoms all of the same mass, but consists of a mixture of two kinds of atoms with respective atomic weights 35 *and* 37.

From the intensity of the lines in mass spectra it is possible to estimate the relative amounts of different isotopes in a complex element and thus to determine the mean atomic weight found by chemical methods.

Table XI gives the number of isotopes of all the elements investigated. We see that an element may have quite a large number of isotopes, e.g. 7 in the case of mercury, 11 for tin. In the latter case there is a difference of 12 units between the atomic weights of the heaviest isotope and the lightest.

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* An extremely feeble line at 18 can be explained as being due to H_2O^+.

TABLE XI.—TABLE OF ISOTOPES

The isotopes are arranged in each case in the order of frequency of occurrence; the radioactive isotopes are indicated by an asterisk. Radioactive isotopes produced artificially are not included.

Element	Z	Isotopes
H	1	1, 2, 3
He	2	4, 3
Li	3	7, 6
Be	4	9
B	5	11, 10
C	6	12, 13
N	7	14, 15
O	8	16, 18, 17
F	9	19
Ne	10	20, 22, 21
Na	11	23
Mg	12	24, 25, 26
Al	13	27
Si	14	28, 29, 30
P	15	31
S	16	32, 34, 33
Cl	17	35, 37
A	18	40, 36, 38
K	19	39, 41*
Ca	20	40, 44, 42, 43
Sc	21	45
Ti	22	48, 50, 46, 47, 49
V	23	51
Cr	24	52, 53, 50, 54
Mn	25	55
Fe	26	56, 54, 57
Co	27	59
Ni	28	58, 60, 62, 61, 56 (?), 64 (?)
Cu	29	63, 65
Zn	30	64, 66, 68, 67, 70
Ga	31	69, 71
Ge	32	74, 72, 70, 73, 76
As	33	75
Se	34	80, 78, 76, 82, 77, 74
Br	35	79, 81
Kr	36	84, 86, 82, 83, 80, 78
Rb	37	85, 87*
Sr	38	88, 86, 87
Y	39	89
Zr	40	90, 94, 92, 96, 91
Cb	41	93
Mo	42	98, 96, 95, 92, 94, 100, 97
Ru	44	102, 101, 104, 100, 99, 96, 98?
Rh	45	103
Ag	47	107, 109
Cd	48	114, 112, 110, 113, 111, 116, 106, 108, 115
In	49	115, 113
Sn	50	120, 118, 116, 119, 117, 124, 122, 121, 112, 114, 115
Sb	51	121, 123
Te	52	130, 128, 126, 125, 124, 122, 123, 127?
I	53	127
Xe	54	129, 132, 131, 134, 136, 130, 128, 124, 126
Cs	55	133
Ba	56	138, 135, 136, 137
La	57	139
Ce	58	140, 142
Pr	59	141
Nd	60	146, 144, 142, 145, 143
Sm	62	144, 147, 148, 149, 150, 152, 154
Eu	63	151, 153
Gd	64	155, 156, 157, 158, 160
Tb	65	159
Dy	66	161, 162, 163, 164
Ho	67	165
Er	68	166, 167, 168, 170
Tm	69	169
Yb	70	171, 172, 173, 174, 176
Lu	71	175
Hf	72	176, 178, 180, 177, 179
Ta	73	181
W	74	184, 186, 182, 183
Re	75	187, 185
Os	76	192, 190, 189, 188, 186, 187
Hg	80	202, 200, 199, 201, 198, 204, 196
Tl	81	205, 203, 207*, 208*, 210*
Pb	82	208, 206, 207, 204, 203?, 205?, 209?, 210*, 211*, 212*, 214*
Bi	83	209, 210*, 211*, 212*, 214*
Po	84	210*, 211*, 212*, 214*, 215*, 216*, 218*
Rn	86	222*, 219*, 220*
Ra	88	226*, 223*, 224*, 228*
Ac	89	227*, 228*
Th	90	232*, 227*, 228*, 230*, 234*
Pa	91	231*, 234*
U	92	238*, 234*

Thus an ordinary element, in the chemical sense, may consist of a mixture of different kinds of atoms. Such an element may be referred to as a *mixed element* or a *complex element.*

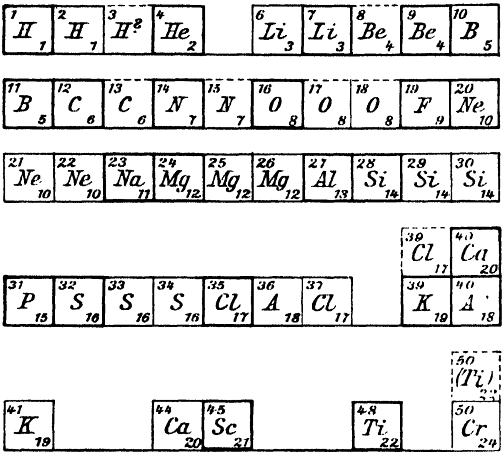

Fig. 6.—The types of atoms with atomic weights from 1 to 50

In some cases it is found that the atoms of chemically different elements have the same mass. Such atoms are called **isobares.*** As may be seen from Table XI and fig. 6, these cases are not very common, and the number of isobares of any given mass never exceeds two. Fig. 7 is a graphical illustration of the relative abundance of the isotopes in an interesting example (anomaly of the chemical atomic weights of potassium and argon).

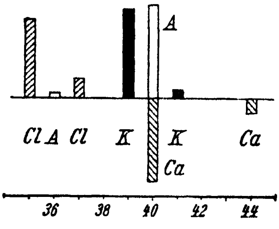

Fig. 7.—Part of the diagram of distribution of atoms with atomic weights from 35 to 44 (relative values). To obtain a quantitative idea of the abundance in meteorites, keep the ordinates for Ca unaltered and diminish those of K by a factor about 10, of Cl by a factor of about 15, of A by a much larger factor. For the distribution in the earth, the corresponding factors are for K unity, for Cl 100, and for A much larger.

It is a remarkable fact that elements of odd atomic number are usually simple or else consist of a mixture of two isotopes at most.

Mass Defect.—Aston's method makes it possible to determine the masses of isotopes with a very high degree of accuracy. It is found that very small deviations from the whole-number rule do occur when oxygen is taken as 16·000. The deviations are all such as to indicate that the actual mass is somewhat less than it would be if the atom under investigation were built up of the appropriate number of hydrogen atoms each of mass 1·00778. The difference between the observed mass and the mass predicted on this hypothesis is called the *mass defect* or *packing fraction.*

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* Gr. *isos*, the same, *baros*, weight.

On the assumption (strongly suggested by the whole-number rule) that the nuclei of the heavier atoms are built up of protons, the existence of these mass defects forces us to the conclusion that the proton must lose a certain fraction of its mass as a result of packing. For further deductions from this remarkable fact see p. 231.

3. The Constituents of the Nucleus

Nuclear Structure.—From the fact that the atomic weight of an element is greater than its atomic number, it follows that nuclei cannot be built up of protons alone. In addition they must contain neutral particles of unit mass. These, of course, cannot be ordinary hydrogen atoms; for the hydrogen atom has a diameter of about 10^{-8} cm., whereas that of the neutral constituents of nuclei must be of the order of 10^{-13} cm. In view of the emission of β-rays in radioactive changes, it has been usual to suppose that nuclei also contain electrons. It must not be forgotten, however, that such electrons as are contained within nuclei must be in a state entirely different from that of the easily removed extra-nuclear electrons or from the electrons in cathode rays or β-rays. We shall therefore speak of *nuclear electrons,* meaning by this the negative constituents which are observed as electrons when they leave the nucleus.

If this view is adopted, then nuclei must be regarded as built up of protons and nuclear electrons, compressed together, in some way as yet unknown, into a region with an effective diameter of about 10^{-12} cm.

Thus the atom of helium, which follows hydrogen in the periodic table and has atomic number 2 and atomic weight 4, is to be regarded as consisting of two extra-nuclear electrons and a nucleus with two elementary positive charges. The nucleus may in turn be regarded as consisting of four protons together with two nuclear electrons. It follows that heavier atoms are very complicated in structure. For example, the radium nucleus (atomic number 88 and atomic weight 226) will consist of 226 protons and $226 - 88 = 138$ nuclear electrons.

In view of the complexity of nuclear structure, it is not surprising that deviations from the inverse square law of force (possibly due to polarization) should be found when a test particle passes very close to a nucleus. Experiments on the scattering of α-particles by the nuclei of light atoms (where the approach is very close on account of the low nuclear charge) actually show such deviations.

The fact that α-particles (helium nuclei) are the only massive particles observed so far in radioactive changes indicates that the complex of 4 protons plus 2 nuclear electrons must be particularly stable (p. 231). Another remarkable fact is that a β-ray change is nearly always followed by a second β-ray change. This indicates that the electrons within a nucleus are arranged in pairs; and the fact that the pairs of β-ray changes are preceded and followed by α-ray changes suggests that the arrangement is such that certain helium nuclei are closely associated with electrons in the nucleus, perhaps thereby constituting neutral α-particles (see also p. 231).

Neutrons.—Considerable light is thrown on these problems by the discovery of the independent existence outside atoms of neutral particles of unit mass (CHADWICK, 1932). These particles discovered by CHADWICK differ radically from hydrogen atoms in that their effective diameter is at most only 10^{-13} cm. They are called *neutrons*. Their properties will be discussed on p. 111. This discovery makes plausible the new view that nuclei are built up of protons and neutrons, and that the very stable α-particle consists of a combination of two protons and two neutrons. It still remains an open question, especially in view of the discovery of the positive electron (p. 114), whether the neutron is to be regarded as a fundamental particle or as a very close association of positive and negative charges.

4. The Relative Abundance of Different Nuclei

The constancy of the observed values of the atomic weights of non-radioactive elements proves the constancy of the proportions in which the isotopes occur in the chemical elements. These definite relative proportions must date from the original formation of the atoms at the birth of the heavenly bodies. We conclude that certain arrangements of the nuclear constituents must be more stable than others, at least under the conditions of formation of the elements, i.e. in the interior of the stars (p. 456). To obtain information about the relative stabilities of the different nuclei, we have therefore to investigate their relative abundance in the universe. Evidence on this point can be obtained only from meteorites. It is to be noted that spectrum analysis of the light from stars is of no avail here, firstly because we can only obtain information about the surface of the stars, and secondly because the intensity of the lines emitted by an element does not bear a simple relation to the concentration of the element. In the same way, investigation of the distribution of the elements on the earth would lead to false conclusions, because the composition of the earth's crust (which is the only part accessible to experiment) must differ from that of the interior. The relative abundance of the different kinds of atom, according to the best evidence meanwhile available, which, however, is by no means conclusive, is shown in fig. 8 on a logarithmic scale. We see that there is a marked decrease in abundance with increasing atomic number (approximately proportional to the seventh or eighth power of the latter).

The first 29 elements form 99·85 per cent of the earth's crust, 99·98 per cent of the stony meteorites, and 100 per cent of the ferrous meteorites. The radioactivity of the elements of high atomic number is additional evidence for the instability of the heavier nuclei.

Taking the nuclear masses as abscissæ instead of the nuclear charges, we obtain fig. 9, which shows the distribution of the lighter elements.

We see from fig. 8 that elements with even atomic numbers are much more abundant than those with odd atomic numbers (Harkins). The two or three elements which have still to be discovered have odd atomic numbers.

If A is the atomic weight (number of protons + number of neutrons) and Z the atomic number (net positive charge on the nucleus), the number of nuclear electrons (or neutrons) must be $N = A - Z$. Inspection of a table of isotopes shows that the number of nuclei for which N is even is about four times the number for which N is odd. In addition, the relative number of nuclei with N even and Z even is about 4 in 7, the relative numbers with N odd and Z even or with N even and Z odd are about equal (taken together about 3 in 7), while hardly any nuclei with N odd and Z odd exist. It is very remarkable that nuclear masses divisible by 4 are particularly abundant. This seems to indicate that the complex corresponding to an α-particle plays a special part in nuclear structure. About 90 per

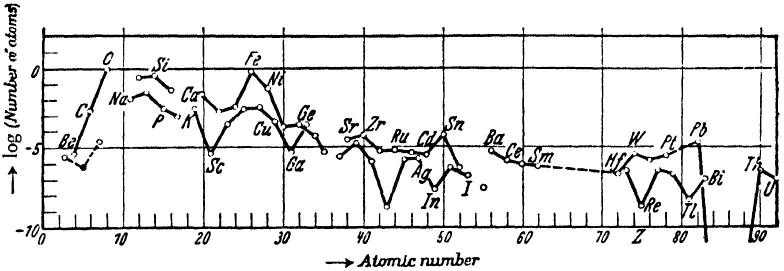

Fig. 8.—Distribution of the elements in meteorites. The distribution in the earth's crust and in the outer layers of stars is in general similar, except for H and He (after Goldschmidt). The elements of odd and even atomic number are joined by separate curves.

[From *Handbuch der Physik*, Vol. XXII (Springer, Berlin).]

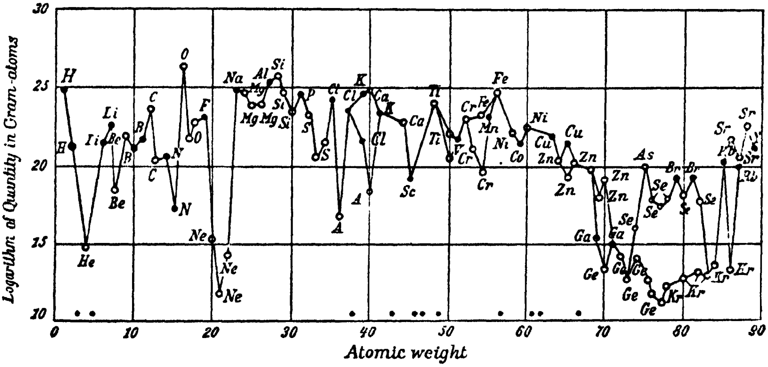

Fig. 9.—Approximate distribution of the lighter elements in the earth's crust

cent of the earth's crust is made up of nuclei whose masses are divisible by 4, viz. O (16), Mg (24), Si (28), S (32), Ca (40), and Fe (56).

In this connexion it is interesting to note that the radioactivity of potassium appears to be entirely confined to the isotope 41 (BILTZ and ZIEGERT).

5. Transmutation of Atoms

Long-range Protons.—When an α-particle collides head-on with a heavy nucleus, it imparts only a small velocity to the latter (see the discussion of elastic collision on p. 89). If, however, the struck nucleus is light, the velocity imparted to it in the collision is correspondingly greater. This is especially marked in the case of hydrogen, where the proton is given a velocity 1·6 times that of the original velocity of the α-particle itself. Now it has been found that the range R of an elementary particle can be approximately represented by the expression $R = Av^3Z^2/m$, where v is the velocity, Z the positive charge, m the mass of the particle, and A a constant. For the direct collision of an α-particle of velocity v_α with a hydrogen nucleus (proton) we have $v_H = 1{\cdot}6v_\alpha$ (v_H being the velocity imparted to the proton), and hence

$$\frac{R_H}{R_\alpha} = \frac{v_H{}^3Z_H{}^2m_\alpha}{v_\alpha{}^3Z_\alpha{}^2m_H} = 4{\cdot}1.$$

Using α-rays with a range of about 7 cm. in air (from RaC′), we should therefore expect to obtain long-range protons with a range of about 29 cm. MARSDEN (1914) actually succeeded in detecting such particles by the scintillation method when substances containing hydrogen were bombarded with α-rays from RaC′. Fig. 10 shows the track of one of these long-range protons. One-half of a radioactive preparation was covered with a thin layer of paraffin. The tracks of the α-rays from the uncovered part are seen on the right of the figure. On the left are the tracks of the α-particles which have been retarded by passing through the paraffin, and also the track of one long-range proton.

In pursuing the investigation of this phenomenon RUTHERFORD discovered (1919) that these long-range particles are produced by the impact of α-particles on nitrogen atoms in complete absence of hydrogen. Together with CHADWICK he subsequently found that the same thing happens with a number of other elements. The particles were identified as protons by the method of magnetic deflection. It was found that some of them had ranges considerably greater (up to 90 cm. for aluminium bombarded with α-rays from RaC′) than that calculated above for hydrogen, and were sent out in the backward direction as well as the forward direction. These facts indicate that the protons must possess energies considerably greater than those of the bombarding α-particles, and that they must be shot out from the struck nucleus in such a way that part at least of their energy is derived from the internal energy of the nucleus. Thus we have an *atomic transmutation*, similar to those which take place spontaneously in the case of radioactive elements.

Bombardment with α-particles (mostly from RaC) has been found to cause emission of protons from all the elements of atomic number up to 19, with the exception of H, He, Li, C, and Be. In these exceptional cases the data are contradictory. The most marked transmutation effects occur with B, N, and Al.

In processes of this kind it seems as though we are not (or not always) dealing with a smashing of the nucleus by the α-particle impact, but rather with a capture of the α-particle. Evidence for this is to be found in the fact that in many cloud-track photographs of transmutations of nitrogen (see fig. 11) only two tracks are produced, that of the long-range proton and that of the rest of the nucleus + the captured α-particle. This explanation corresponds to the formation from nitrogen (atomic weight 14, atomic number 7) of an atom of atomic weight 17 and atomic number 8, i.e. the oxygen isotope 17. This isotope has actually been detected spectroscopically in the earth's atmosphere.

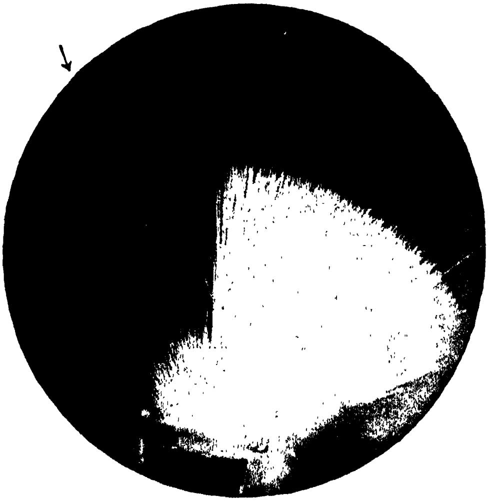

Fig. 10.—Track of a long-range proton produced by bombardment of paraffin with α-rays. (The track is indicated by the arrow on the left)

[From L. Meitner, *Die Naturwissenschaften*, 1927 (Springer, Berlin).]

The number of direct head-on collisions of α-particles with nuclei in any experiment is very small, only one long-range proton being produced for several hundred thousand α-particles. Now it can be calculated from the number of ions produced that an α-particle actually passes through some 100,000 atoms in the course of its range. Hence it follows that only about one in 10^{10} of such passages through atoms results in a nuclear transmutation. It is found quite generally that above a certain limiting velocity (for boron about that corresponding to a range of 1·3 cm., for nitrogen about 2·8 cm.) a bigger yield is obtained. It appears further (according to Pose) that for the different kinds of atoms there are different velocities of the bombarding α-particles which produce particularly large yields (so-called resonance transmutation).

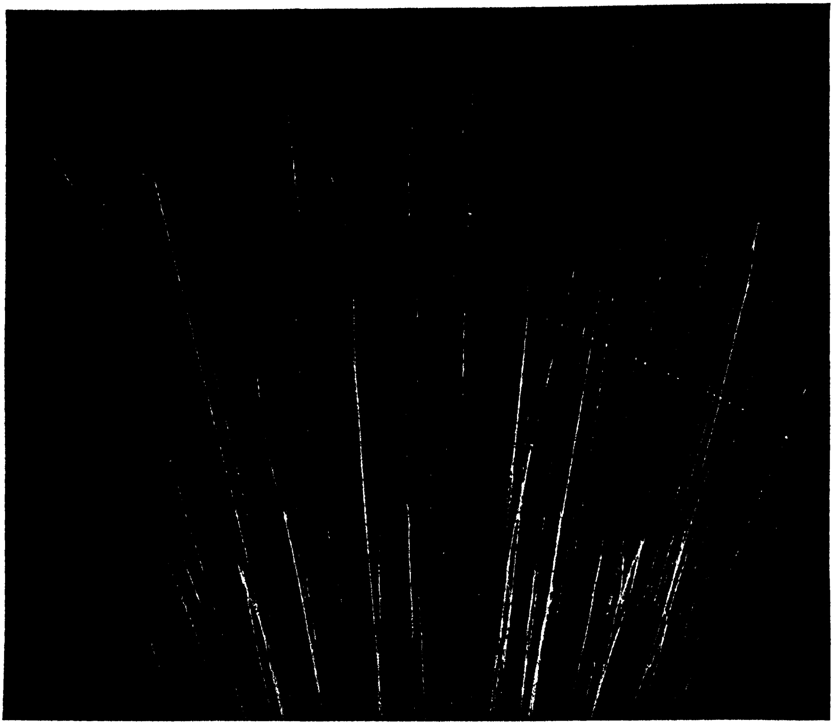

Fig. 11.—Cloud-track photograph showing the transmutation of a nitrogen nucleus by the capture of an α-particle and emission of a proton (after Blackett)

[From *Handbuch der Physik*, Vol. XXII, 1 (Springer, Berlin).]

Transmutations of atoms can also be brought about by bombardment with protons which have been accelerated in a high electric field. This was first shown by Cockcroft and Walton in 1932, using a potential fall of about 120,000 volts. They found that the lithium atom was disrupted with emission of α-particles, probably in accordance with the equation $Li^7 + H^1 = 2He^4$, in which the masses of the particles are written as indices. A number of other elements were also transmuted in the same way. Here again the yield increases with the energy of the protons. By improving the methods of detection RAUSCH VON TRAUBENBERG has succeeded in demonstrating that lithium is transmuted even by protons accelerated by a potential fall as low as 13,000 volts; but here the yield is only one in 10^{17}.

As has been shown by BOTHE and BECKER (1930), a short-wave electromagnetic radiation (corresponding to the γ-rays of radioactive elements) is also produced by the α-ray bombardment of light elements (particularly Li, B, F, and above all Be).

The Neutron.—The transmutation experiments described above show that the proton really is a fundamental constituent of the nucleus. Protons, electrons, and α-particles, however, are not the only constituents.

Closer investigation of the effect of bombarding beryllium with α-particles gave a very remarkable and unexpected result. Madame CURIE-JOLIOT and M. JOLIOT found in 1932 that rays are produced which, when allowed to fall on substances containing hydrogen, in their turn produce new strongly-ionizing particles, with the properties of protons with a velocity of about 3×10^9 cm. per second. CHADWICK was also able to show (1931) by means of an ionization chamber that the rays emitted from bombarded beryllium give rise to rapidly-moving atoms when allowed to fall on other elements, e.g. He, Li, Be, C, O, N, and A. Difficulties are encountered if an attempt is made to explain these effects as due to an electromagnetic radiation (p. 235); in particular, the dependence of the velocities of the atoms upon their masses is different from what one would expect on this view.

The ranges of the moving atoms observed by CHADWICK in different elements subjected to the rays from bombarded beryllium can be satisfactorily explained on the view that the particle colliding with them has a mass equal to that of a proton. Quite unlike the well-known high-speed protons, however, the particles in question produce no tracks in the cloud-chamber and no ionization in the ionization chamber. These facts, together with their extremely high penetrating power, indicate that their charge must be zero. That is, they are *neutral particles of unit mass*. These particles are called *neutrons*. The possibility of the existence of such particles had been considered much earlier by LENARD (nuclear dynamids) and by RUTHERFORD (1920). From the lengths and total ionization of the tracks of struck nuclei information can be obtained about the velocity of these nuclei and hence about the velocity of the impinging neutrons. The value found for neutrons from bombarded beryllium is about a tenth of the velocity of light.

Since neutrons appear to be at most of the same dimensions as nuclei, they are practically unaffected in passing through the outer parts of atoms and produce practically no ionization. Only when they collide directly with a nucleus or with an electron does their presence become apparent. The struck particle recoils and produces ionization along its track, thereby betraying the existence of the neutron which struck it. A photograph of such a recoil track, produced by a particle struck by a neutron, is shown in fig. 12.

The velocity v imparted to an originally stationary body of mass m by the direct impact of another body of mass m_0 and original velocity v_0 is given by $v = 2m_0v_0/(m_0 + m)$ (see Vol. I, p. 215, and this volume, p. 89). Hence the maximum velocity attainable by the struck body is $2v_0$, when the impinging body is of infinite mass ($m \ll m_0$).

Thus the velocity imparted to an electron by the direct impact of a neutron cannot exceed twice the original velocity of the neutron.

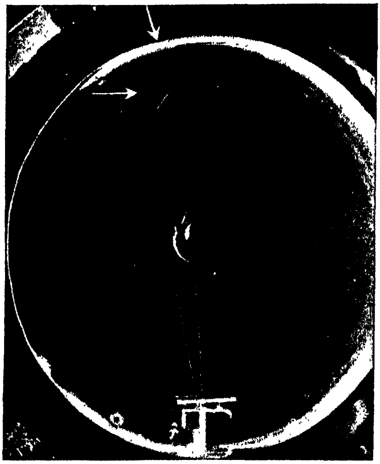

Fig. 12.—Recoil of a He nucleus after collision with a neutron. In the centre is the α-ray source surrounded by a beryllium sheath. Below is a control preparation with α-particle tracks (after Rasetti).

[From *Die Naturwissenschaften*, 1932 (Springer, Berlin).]

If we use neutrons with a velocity of about 3×10^9 cm. per second, this means that the electron tracks (which can be distinguished by the nature of their ionization from the tracks of massive particles) will be quite short. These short electron tracks (similar to short-range β-ray tracks) have actually been observed by Chadwick, Feather, and Dee on more than a hundred cloud-track photographs in which neutrons from beryllium were allowed to pass through the chamber. The observed lengths are in good agreement with the theory.

Further evidence for the nature of the neutron is the fact that the ranges of the struck atoms are reduced if the neutron beams are first made to pass through a layer of matter. This behaviour favours the view that neutrons are corpuscular, rather than undulatory, in their nature.

The CURIE-JOLIOTS and DEE have also observed tracks of faster electrons, such as one might expect to be produced by γ-rays. Thus it seems that γ-radiation is emitted in the transmutation of beryllium, in addition to the neutron rays. From an investigation of ionization by neutrons in counting apparatus RASETTI has also been led to the conclusion that γ-radiation with an $h\nu$-energy of 10 million electron-volts must also be present.

The process in which the neutrons are expelled from the beryllium nucleus is probably to be regarded as a capture of the α-particle by Be^9 with simultaneous formation of C^{12}: thus $Be_4{}^9 + He_2{}^4 \rightarrow C_6{}^{12} + n_0{}^1$. In this equation the nuclear masses are indicated by indices and the corresponding charges by suffixes. The neutron is denoted by $n_0{}^1$.

As RUTHERFORD has concluded from cloud-chamber tracks, FEATHER (1932) has further succeeded in producing new types of transmutation of nitrogen nuclei by bombardment with neutrons. He obtains two types: one involving capture of the neutron and emission of an α-particle, and the other involving the knocking-out of a proton without capture of the neutron.

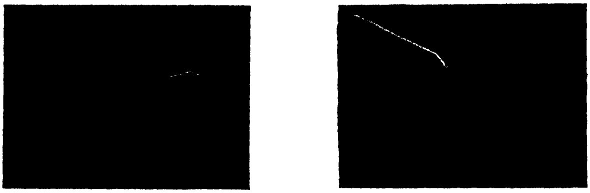
Fig. 13.—Nitrogen Fig. 14.—Oxygen

Figs. 13 and 14.—Atomic transmutations due to bombardment by neutrons

[From *Die Naturwissenschaften*, 1932 (Springer, Berlin).]

Fig. 13 shows a transmutation of the nitrogen nucleus according to the equation $N^{14} + n_0{}^1 \rightarrow B^{11} + He^4$. The shorter track (range 3·3 mm.) belongs to the boron nucleus; the longer track (range 10·1 mm.) belongs to the α-particle. The neutron produces no cloud-track (see below), but its direction of motion can be obtained by joining the source to the point of collision. Measurement of stereoscopic photographs and application of the laws of conservation of energy and momentum make it possible to calculate the original energy of the neutron, the value obtained being $3{\cdot}4 \times 10^6$ electron-volts; of this, $0{\cdot}42 \times 10^6$ electron-volts are absorbed in the collision. Fig. 14 shows the transmutation of an oxygen nucleus: $O^{16} + n_0{}^1 \rightarrow C^{13} + He^4$. In this photograph the shorter track (range 6·6 mm.) belongs to the C^{13} nucleus and the longer track (range 28·3 mm.) to the α-particle. The original energy of the neutron comes out as $8{\cdot}3 \times 10^6$ volts, of which $0{\cdot}9 \times 10^6$ volts are used up in the collision. It is interesting that α-particle bombardment of boron gives nitrogen with emission of neutrons, while (as we have just seen) neutron bombardment of nitrogen gives boron with emission of α-particles. Thus this process can be carried out in the laboratory in both directions.

A remarkable property of neutrons is their very great penetrating power. Whereas a proton of velocity 3×10^9 cm. per second has a range of only 30 cm. in air, the range of a neutron of the same velocity is several miles in air. This statement is based upon actual absorption measurements. We conclude that the dimensions of the neutron and the extent of its field must be very small (10^{-12} to 10^{-13} cm.). This explains the fact that the ionization produced by neutrons is extremely small—only one ion-pair for several metres of path—and that no appreciable cloud-track is formed (see figs. 12, 13, and 14). The yield of neutrons is of the same order as the yield of high-speed protons by the appropriate nuclear transmutations. The most favourable source, beryllium bombarded by the α-particles from polonium, gives only about 30 neutrons per million α-particles. The yield is increased by using α-particles of higher energy. All the elements up to aluminium appear to give neutrons, with the exception of He, N, C, and O. A few elements, e.g. F and Al, give both neutrons and protons.

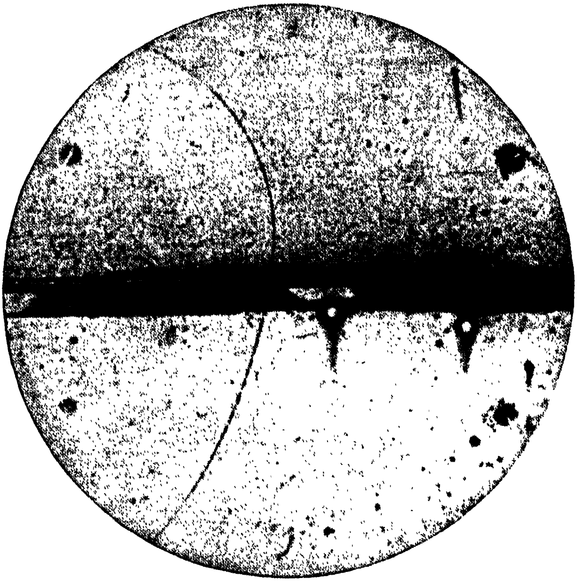

Fig. 15.—Cloud-track of a positive electron in a magnetic field
[After Anderson, *Physical Review*, Vol. XLIII, 1933]

The Positive Electron.—In the course of cloud-chamber investigations of the particles produced by the action of so-called cosmic radiation upon matter, ANDERSON discovered new positive particles along with negative electrons. Their charge and mass were determined from their magnetic deflection and the ionization they produced. The particles proved to have about the same mass as ordinary electrons; but their charge, though equal in magnitude to the electronic charge, is opposite in sign.* They have been given the name of **positive electrons** or **positrons.** Positron tracks are shown in figs. 15 and 16. By the adoption of a special device BLACKETT and OCCHIALINI have succeeded in photographing a large number of positive electron tracks and so determining the charge and mass of the particles. Often a " shower " of positrons is observed, the tracks all originating from a single point (fig. 17). Such showers indicate that some kind of nuclear explosion must have occurred. It was later found possible to produce positrons

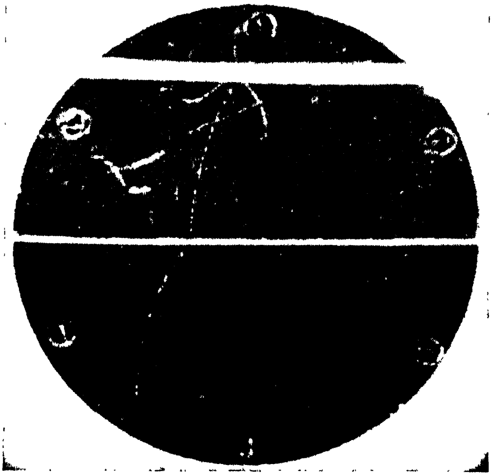

Fig. 16.—Cloud-track of a positive electron in a magnetic field of 430 gauss. The positive electron was produced by irradiation of lead with γ-rays from RdTh and its disintegration products (after Anderson). At the top is the lead plate, across the middle is a sheet of aluminium. Assuming the mass of the particle to be the same as that of an ordinary negative electron, the velocity above the aluminium sheet comes out as 820,000 volts, below the aluminium sheet as 530,000 volts. [From *Physical Review*, Vol. XLIII, 1933.]

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* Of course a simple magnetic deflection experiment does not differentiate between a positive electron and a negative electron travelling in the reverse direction. To settle this point, the particles in question were caused to pass through a layer of matter (the aluminium plate of fig. 16), and the curvatures of their tracks in a magnetic field were measured on both sides. Passage through matter will obviously slow down the particles; hence the curvature must be greatest on the side of emergence. An observation of this kind thus makes certain the sense in which the particles are moving, and so removes any possible ambiguity as to the sign of their charge. Further evidence is provided by the fact that the particles are sometimes observed in " showers ", the corresponding tracks all radiating from a single point. The sense of motion must obviously be away from this point, as it is scarcely conceivable that so many particles should converge upon one spot.

by irradiating lead with the very short-wave γ-rays of ThC″. So far this field of investigation has scarcely been touched, and no more detailed experimental data on the nature of the underlying elementary processes are available.

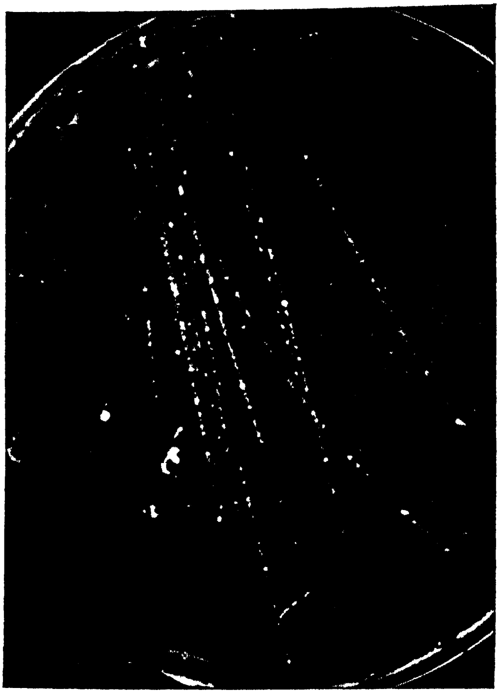

Fig. 17.—Shower of particles (positive and negative electrons and nuclei) produced by cosmic rays. (Taken in a magnetic field.)

[After Blackett and Occhialini, *Proc. Roy. Soc.*, A, Vol. CXXXIX, 1933.]

Closely related to the discovery of the positron is the question whether the neutron is of a complex or an elementary nature. The neutron may be regarded as an elementary neutral particle or as a very close association of a proton and a negative electron.

If nuclei are built up of protons and neutrons (p. 106), the fact that β-rays are emitted seems to favour the latter view. An important point is that this β-ray emission from the nucleus has a continuous velocity spectrum (p. 20). But the original and final states of the nucleus are definite, so that we should expect the β-ray velocity, or energy, to be also definite. To meet this difficulty Pauli and Fermi have postulated the existence of a new particle within the nucleus. The particle has been called the *neutrino*. It is supposed to have no charge and only a very small mass. Its function is to preserve the conservation of energy.

CHAPTER III

Light and Matter

A. THE PHOTOELECTRIC EFFECT

1. The External Photoelectric Effect

It has already been mentioned in Vol. III (p. 312) that if the cathode of a vacuum tube is illuminated with light of sufficiently short wavelength, a current flows when a relatively small potential difference is applied. This current is due to electrons liberated from the cathode by the action of light. The cathode may be made of any metal or material which exhibits metallic conduction. (For other substances see p. 125.)

Historical.—The discovery of this effect goes back to an observation of H. Hertz (1887), who found that the passage of a spark between metallic electrodes is facilitated by illumination with ultra-violet light. In 1888 Hallwachs showed that this is associated with the production of carriers of electricity; the fact that these carriers are electrons was established in 1899 by Lenard (Vol. III, p. 318).

An experiment similar to that mentioned above is illustrated in fig. 1. Here the space between the electrodes of a charged condenser is filled with a transparent insulator of high refractive index ($n > 2$; zinc blende, diamond). If zinc blende is used, the distance between the electrodes should be about 1–2 mm. When the insulating medium between the electrodes is illuminated, a current is observed (see fig. 1). This is clearly due to the liberation of carriers of electricity in the interior of the dielectric. The originally charged condenser discharges itself, as is seen by the fall of potential shown by the electrometer connected in parallel with it.

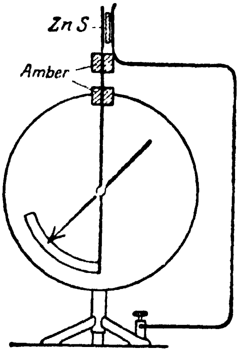

Fig. 1.—Apparatus for showing the motion of electric charges in a crystal on illumination (after Pohl).
[From R. W. Pohl, *Physical Principles of Electricity and Magnetism* (Blackie & Son, Ltd., 1930).]

Thus on the one hand we have an *external photoelectric effect* occurring at the surface of solids or liquids, and on the other hand an *internal photoelectric effect* occurring in their interior.

Fundamental Experiments.—In the experiment described in Vol. III, p. 312, a current is observed in the external circuit even when no potential difference is applied, provided that the tube is well evacuated and the wave-length of the light used to irradiate the electrode is sufficiently short; the irradiated electrode becomes the cathode. It follows that the electrons liberated by the light must leave the electrode with a certain velocity. In actual practice it is very difficult in this form of the experiment to fulfil the condition that there shall be no potential difference between the electrodes when there is no illumination; for as a rule there will be a contact potential difference amounting to several tenths of a volt or even to several volts.

The liberation of individual electrons can be very clearly followed by the balanced-drop method described in Vol. III, p. 47. A particle suspended in the field of a Millikan condenser is irradiated from the side with light of short wave-length (e.g. with X-rays, as in fig. 53, Vol. III, p. 48). It is then possible to observe the sudden changes in the charge of the particle, and to show by measurement that these changes correspond to the loss of a single electron. By using suspended particles of differing substances it can be shown that the photoelectric effect is common to both metals and insulators. With extensive layers of insulating material, however, the effect is reduced practically to zero, owing to the charging-up which occurs.

Connexion between the Number of Electrons and the Intensity of the Light.—As long ago as 1892 ELSTER and GEITEL proved that the number of electrons liberated by illumination with light of definite spectral composition is directly proportional to the absorbed light intensity, and hence also, if the conditions are kept constant, directly proportional to the incident light intensity. To obtain this result it is necessary to use a very good vacuum and to eliminate all possible sources of error (p. 128). The relationship is then found to hold good for alterations of light intensity in ratios up to $1:10^9$. Upon it depends the possibility of using the photoelectric effect to measure light intensities (p. 127).

If only the absorbed light energy is considered, it is found (POHL, 1909) that the number of electrons liberated (so-called *photo-electrons*) is completely independent of the angle of incidence and state of polarization of the light. Marked differences may well occur when the *incident* intensities are equal, owing to unequal absorption and reflexion. The decisive quantity is always the *absorbed energy*.

Velocity Distribution of Photo-electrons.—The conductivity observed in the experiment of Vol. III, fig. 18, p. 312 having been proved to be due to electrons, the velocity of these electrons can be determined from the radius of curvature of their paths in a magnetic field. For this it is necessary to work *without* any potential difference between the electrodes of the tube. For more accurate determinations the form of apparatus shown in fig. 24, p. 44 is used (**Ramsauer**'s method). A narrow circular path is determined by suitably arranged slits 1, 2, 3, . . . (see fig. 24). The uniform magnetic field is applied in such a way that the lines of force are at right angles to the plane of the figure. By suitable regulation of the field strength and simultaneous observation of the number of electrons entering the collecting cage at 8 (by noting the rate of charging of an electrometer), a measure is obtained of the relative numbers of electrons liberated from the illuminated plate (marked Zn in the figure) with velocities determined by the radius of the path and the respective strengths of the applied magnetic fields.

A second method of investigating the velocities of the electrons depends upon the application of a retarding field (**Lenard**). Fig. 2 is a diagram of a radially symmetrical arrangement of this kind. The substance M under investigation is placed at the centre of a large hollow conducting sphere H, which is not photoelectrically sensitive to the radiation used. The whole is completely evacuated. Light falling on M through a small window liberates electrons, which all travel to H when there is no retarding field. The current produced in this way can be measured by an electrometer connected as shown. Application of an accelerating potential between M and H (i.e. H is made positive relative to M) makes no difference to the current strength, for the latter already has its saturation value, since all the electrons reach H. If, however, a retarding potential is applied, only those electrons with initial velocities (expressed in volts) greater than the applied potential will be able to overcome the opposing field and reach the sphere. Actually the electrons liberated by the photoelectric effect have various velocities, so that the effect of increasing the retarding field will be to diminish the observed current gradually (see fig. 3). The gradual increase in the applied potential can be conveniently brought about by means of a potentiometer arrangement like that shown in fig. 2.

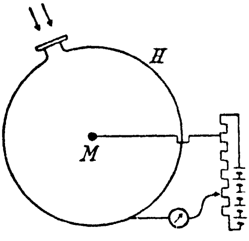

Fig. 2. — Retarding field method with spherically symmetrical arrangement.

Electrons with volt-velocities less than the potential difference of the applied retarding field are turned back before reaching H and return to M, just as a stone thrown upwards falls back to the ground. It is not difficult to see that the rate of fall of the curve of fig. 3 (i.e. its gradient or derivative at any point) is a direct measure of the number of electrons which just fail to reach the sphere H for the particular value of the retarding potential.

The retarding potential at which the current becomes zero gives the maximum electron velocity occurring under the conditions of the experiment. When the current is zero, all the electrons are turned back by the field and return to M.

Differentiation of the ordinate in fig. 3 gives the velocity distribution of the electrons, i.e. the relative numbers of electrons with velocities within given ranges (compare fig. 31, p. 49, and fig. 6, p. 123).

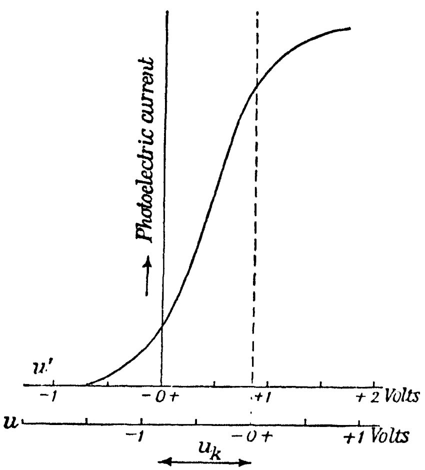

Fig. 3.—Photoelectric current at different retarding potentials

u' = measured potential of anode relative to cathode. u = true value, corrected for contact potential difference u_k.

In order to obtain the maximum electron velocity another method due to Lenard may also be used, in which the quantity observed is the potential (relative to the surroundings) eventually taken up by the body under investigation when very carefully insulated and exposed to the illumination. Thus in this method the retarding field is set up by the loss of the photo-electrons themselves, and the final potential reached (the insulation being assumed perfect) is that at which even the fastest electrons are unable to get away from the illuminated body and fall back again to it along parabolic paths.

Independence of the Maximum Velocity of the Photo-electrons and the Intensity of the Incident Light.—In 1902 Lenard discovered the fact, then completely unexpected, that *the maximum velocity of the electrons liberated by a definite kind of light is independent of the incident intensity.* This discovery has proved of fundamental importance in the subsequent developments of atomic physics. Table XII gives the relative values obtained by Lenard

Table XII.—Variation of the Maximum Velocity of the Photo-electrons with Light Intensity

Light intensity (in arbitrary units)	Maximum velocity in "volts"
276	1·05–1·10
174	1·12
32	1·10
4·1	1·06

with a carbon arc. Other experiments have shown that this independence of incident intensity and electron velocity holds not only for the maximum velocity but also for the whole velocity distribution.

Variation of the Velocity with the Frequency of the Light.—In the course of the same investigations Lenard found indications of a variation of the velocity of the emitted electrons with the wave-length of the light used, in the sense that the velocity increased as the wave-length was made shorter. More accurate investigations of this point were not made till some ten years later (Hughes, 1912); the matter was then taken up in particular by Millikan (1916). On account of the great importance of the results, these experiments will now be discussed in greater detail.

The surfaces under investigation are mounted in a high vacuum in such a way that they can be cleaned and interchanged *in situ*. The exciting light must be very carefully freed from all stray light, especially that with a shorter wave-length. This may be effected by means of a double monochromator, i.e. two stages of spectral decomposition by means of prisms. The maximum velocity of the photo-electrons is determined by observing the value of the retarding potential at which the current between the irradiated substance and an auxiliary electrode just becomes zero. Fig. 4 exhibits these retarding potentials as determined by Millikan for differing incident wave-lengths. We see that as the wave-length is diminished the retarding potential for zero current increases, i.e. the velocity of the electrons on leaving the surface increases. To find the actual electron velocities, it is necessary to make allowance for the contact potential difference between the substance under investigation and the auxiliary electrode. In the case of fig. 4 (sodium) this involves a correction of 2·47 volts. The corrected potentials are given on the lower horizontal axis on the figure. The maximum velocities are given by the points where the curves meet the horizontal axis. They are plotted in fig. 5 as a function of the frequency of the light used. The graph obtained is a straight line; its equation may be written in the form

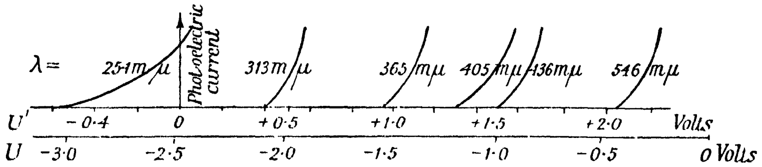

Fig. 4.—Variation of photoelectric current with retarding potential at different wave-lengths in Millikan's experiment

U′ = measured potential of anode relative to cathode.
U = potential corrected for the contact potential of −2·47 volts.

$$(\tfrac{1}{2}mv^2 =) \quad eU_{\max} = h\nu - p,$$

where $eU_{\max}$ is the maximum electron energy, ν is the frequency of the light, and h and p are constants. The threshold of the photoelectric effect is given by the point where the line meets the frequency axis, for here the maximum velocity is zero. In the present example of sodium the frequency of this threshold is $\nu = 4{\cdot}39 \times 10^{14}$ sec.$^{-1}$, which is equivalent to a wave-length of $\lambda = 683 m\mu$.

In the above equation p means the amount of energy required to remove an electron from the substance in question. This we may call the **work of separation.**[*] In general it consists of two parts, the **energy of ionization** required to split off the electron from the atom, and the energy required to get it out through the surface of the body (the so-called **work function**[†]). The value of p generally amounts to a few electron-volts.

The great significance of this equation, especially that due to the occurrence in it of the universal constant $h = 6{\cdot}55 \times 10^{-27}$ erg sec., will be realized in the course of the discussion of other facts in atomic physics.

Quanta of Energy and Light.—The energy properties of light in the photo-electric effect were given a theoretical basis by Einstein in 1905, after Planck had put forward his theory of the quantum behaviour of atomic resonators (p. 148). Einstein's theory, which was based upon the experimental results of Lenard, has been amply justified by subsequent work. The photoelectric effect obviously consists in the transference of the energy of the absorbed light to an electron. This energy then appears (except for the amount p) as kinetic energy of the electron. It is observed, however, that the kinetic energy is independent of the intensity of the incident light, and depends only on the frequency. Accordingly we may associate with the light a certain energy of magnitude $h\nu$, such that the transferences of energy to the substance in the photoelectric effect can only take place in integral multiples of this amount. The quantity of energy $h\nu$ can be communicated to an electron in some way still unknown, whereby the electron is given a certain kinetic energy. The magnitude of this kinetic energy cannot exceed $h\nu$, but may be less than $h\nu$ if part of the energy is used up in other ways.

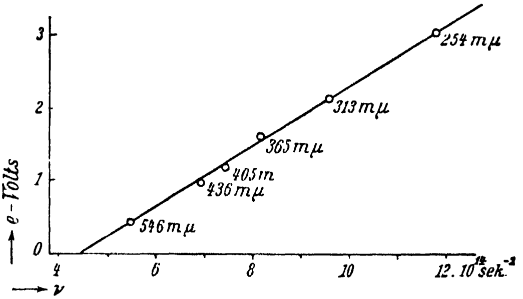

Fig. 5.—Maximum electron energy (from fig. 4) as a function of the frequency

We may therefore regard the energy carried by the light as concentrated in packets, each of magnitude $h\nu$ and each behaving individually and independently. These energy packets are called **light quanta** (see Vol. IV, p. 1). For further properties of light quanta see p. 233.

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[*] Ger. *Abtrennungsarbeit.*

[†] Ger. *Austrittsarbeit.*

Velocity Distribution with Monochromatic Illumination.—Even when the light used is all of one frequency, the emitted electrons leave the surface with different velocities. This fact is possibly due to the different paths taken by the electrons before they arrive at the surface. This has been demonstrated in particular by the sphere method of fig. 2, p. 119, in which the magnitudes of the velocities are measured directly, since the electrons always travel in the direction of the field, no matter at what angle they emerge from the surface. It is found that the energies are distributed about a maximum as shown in fig. 6. The distribution about the maximum is independent of the particular frequency used, so that for the average energies there is also a linear dependence upon the frequency.

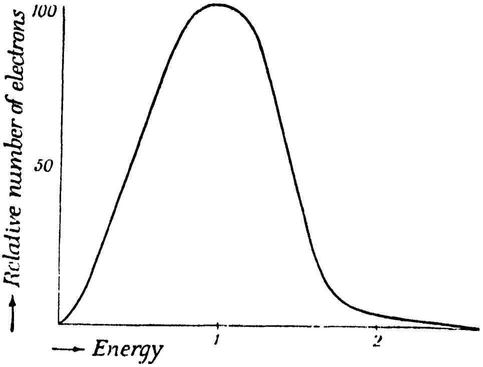

Fig. 6.—Distribution of kinetic energy of photo-electrons from zinc (after Ramsauer). The relative shape of the curve is the same for all wave-lengths (measured from 285 to 186 $m\mu$).

Spectral Distribution of the Photoelectric Effect.—Experiments show that the electron yield (i.e. the number of photo-electrons passing through the surface, referred to the same amount of absorbed energy in all cases) depends very much upon the wave-length of the light. In this connexion we distinguish between two cases: the so-called **normal photoelectric effect,** in which the number of electrons increases with increasing frequency, and the so-called **selective photoelectric effect,** in which the yield is a maximum at a certain frequency. Examples of these two cases are given in figs. 7 and 8 respectively.

Normal Photoelectric Effect.—The number of photo-electrons (per unit absorbed energy) increases with increasing frequency. Most of the measurements refer to layers of material which are very thick relative to the actual absorbing layer, so that it is certain that only a fraction of the electrons liberated in the interior are actually observed. In these cases the nature of the surface has a very great influence. The presence of layers of gases, on the surface or absorbed in the interior, is of importance, especially for the long-wave threshold, which (according to different observers) may vary by 100 mμ or more for the same "pure" metal. Changes of photoelectric sensitivity with time ("fatigue" effects) may also be explained by the gradual formation of such layers. In general we may say that every metal shows a photoelectric effect from a long-wave threshold of 300–200 mμ onwards. In some cases, however, the long-wave threshold may lie in the infra-red, e.g. for some compounds which exhibit metallic conduction, and for strongly electro-positive metals, such as rubidium.

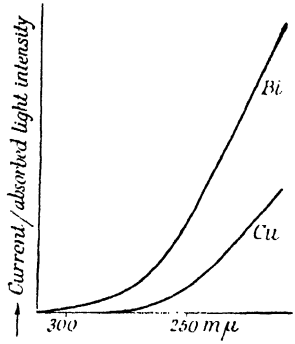

Fig. 7.—Normal photoelectric effect

Selective Photoelectric Effect.—Some metals (and probably also some compounds) exhibit the behaviour illustrated in fig. 8, i.e. give a well-marked maximum of photoelectric sensitivity at a certain frequency. Working with polished mirror surfaces, Pohl and Pringsheim were able to show in 1910 that these selective effects occur

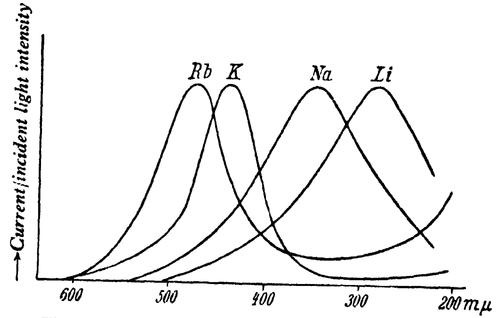

Fig. 8.—Selective photoelectric effect in alkali metals

only when the electric light vector possesses a component normal to the metal surface. Fig. 9 gives the experimental results. We see that the selective effect is obtained when the light is such that there is an electric component normal to the surface, but that the normal effect is alone obtained in the absence of such a component. The selective effect in the first case is superimposed upon the normal effect. The position and height of the maximum are greatly influenced by structure and the condition of the surface. Probably the selective effect depends entirely on some peculiar surface condition exhibited by alkali and alkaline-earth metals. For the photoelectric effect of phosphors see p. 173.

Occurrence of the Photoelectric Effect.—Probably all solid substances would give the effect with light of sufficiently short wave-length, provided only that the light were absorbed. In this connexion account must be taken of the static charging of insulators. Apart from the metals, but few substances have been investigated. Amongst these may be mentioned organic dyes, for which no connexion between fluorescence and the photoelectric effect is found, also various halogen compounds ($<200\ m\mu$) and ice ($<180\ m\mu$). Among aqueous solutions, potassium ferrocyanide alone gives an appreciable effect above 180 $m\mu$. Specially detailed investigations have been carried out upon the phosphors CaS and SrS in the form of powder (p. 173). These show selective maxima at the regions of exciting absorption and a general photoelectric sensitiveness increasing towards the shorter wave-lengths, corresponding to the so-called ultra-violet process (non-selective excitation) of phosphorescence.

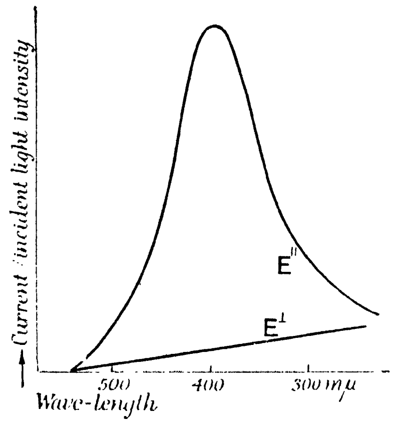

Fig. 9.—Influence of polarization on the photoelectric effect of a Na-K alloy. Angle of incidence 60°.

(E = electric vector parallel to plane of incidence. $E^{\perp}$ = electric vector normal to plane of incidence.)

The Quantum Yield.—It has been stated on p. 122 that when the energy of absorbed light is transferred to electrons, the transference takes place in quanta of magnitude $h\nu$ (where ν is the frequency). If one quantum is transferred to each electron, it follows that the number n of electrons liberated by a total quantity Q of absorbed light energy is given by

$$n = \frac{Q}{h\nu}.$$

This number is called the **quantum equivalent.** From the equation it follows that the number of electrons liberated per unit of absorbed light energy is inversely proportional to the frequency of the light; but as the number of electrons falls off, the energy imparted to each of them becomes correspondingly greater (the work of separation p being regarded as constant).

If we imagine the energy of the light concentrated in some way into quanta each of magnitude $h\nu$ (see p. 233 and Vol. IV, p. 1), the above relation states that the number of such quanta making up the energy Q is inversely proportional to the frequency of the light. The amount of energy $h\nu$ in a quantum is directly proportional to the frequency ν.

The electron yields (i.e. the numbers of electrons per unit of energy, here per watt-second) to be expected in view of the above relationship are plotted in fig. 10 (the continuous line). The point at which the line stops is determined by the work term p; for when $h\nu$ becomes equal to p the quantum energy is no longer large enough to eject an electron. Comparison with fig. 7 (p. 124) shows that the actual curves observed for the normal photoelectric effect in metals slope in quite a different way. Yet no contradiction of our principles is involved, as we see when account is taken of the actual values of the ordinates. In fig. 7 the observed yield does not amount even to a thousandth of that which we would expect from quantum considerations. Thus less than a thousandth of the absorbed light energy is transformed into kinetic energy of electrons passing out from the surface, if due allowance is made for the work p used up in separating the electrons from the material in question. Hence in the course of the transformation of the light energy in the interior, processes must occur which use up the energy in other ways, converting it eventually into thermal motions.

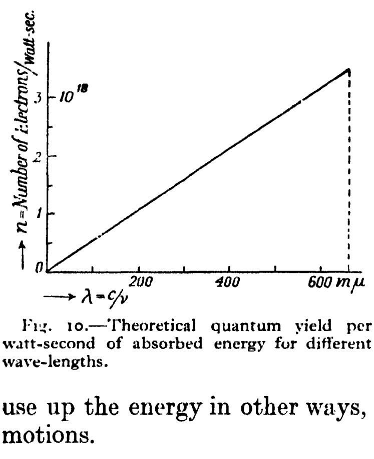

Fig. 10.—Theoretical quantum yield per watt-second of absorbed energy for different wave-lengths.

In the first place it is probable that the directions in which the electrons are emitted from the absorbing atoms are distributed more or less at random, so that only a fraction of the electrons actually liberated is susceptible to observation. Further, only a fraction of those emitted in the right directions are able to reach the surface of the material with a sufficiently high normal velocity component. Of very great importance in this connexion is the condition of the outermost layers of the surface, especially their capacity for allowing electrons to pass through. This explains the enormous importance of surface condition for photoelectric yield. It is easy to see that electrons with higher initial velocities will penetrate the surface in greater numbers. Hence the rise of yield with increase of frequency, at least as far as it has hitherto been experimentally realized —a fact which at first seems to contradict the deductions from the quantum theory. It is not impossible, however, that with longer wave-lengths the matter may be complicated by modification of the nature of the absorption process, whereby only a fraction of the absorbed light is photoelectrically effective.

If only the effects of internal absorption and surface discontinuity could be eliminated, it would be possible to demonstrate the full quantum equivalent. As will be explained on p. 130, this has actually been achieved in certain cases.

Photoelectric Cells.—The practical application of the photoelectric effect depends on the transformation of light energy into electrical energy in a cell like that illustrated in fig. 11. The photoelectric cell consists of a sealed bulb of glass or silica, in which are mounted the photo-sensitive layer (usually a specially prepared film of alkali metal) and an auxiliary electrode. Leads are sealed into the bulb and connected to terminals. In general an auxiliary potential difference is applied between the electrodes, the sensitive layer being made negative. The electrical energy is then derived from the auxiliary battery, the actual cell acting only as a control. The electron current liberated by the incident light is exactly proportional to the light intensity (p. 118). Light flashes as brief as 3×10^{-9} sec. produce an immediate response, the action of the cell being entirely devoid of inertia.

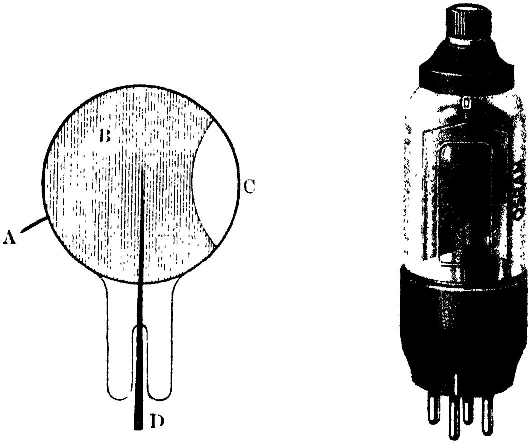

Fig. 11.—Photoelectric cell as used in practice

In the case of a well-evacuated cell the whole current is a pure electron current. Here very small applied potentials are sufficient to raise the current to its saturation value, after which further increases in potential produce no further effect. The actual currents obtained, however, are small, of the order of 10^{-10} ampere per lux of incident energy.

In order to increase the current, the cell is sometimes filled with an inert gas. Increase of applied potential then causes a large increase in the ionization produced by the accelerated electrons, thereby increasing the number of carriers and thus increasing the current.

Fig. 12 shows the current-voltage characteristics of a vacuum photo-cell (curve I) and a gas-filled cell (curve II). In the first case saturation is reached with relatively low applied potentials. In the second case the current rises rapidly; but when a certain applied potential is exceeded, spontaneous discharge sets in, with consequent damage to the cell. A disadvantage of these cells is the occurrence of fatigue effects, e.g. a decrease in sensitiveness after strong illumination. Quantitative work with photoelectric cells therefore requires some care and experience. For the short-wave ultra-violet region use is made (especially in meteorology) of cadmium cells; for longer wave-lengths the selective effects of alkali metal films are used. With gas-filled cells and great light intensities it is possible to use a galvanometer to measure the current; but with vacuum cells and lower intensities a very well insulated electrometer must be used. Another method is to connect the photoelectric cell to the grid of an amplifying thermionic valve (or system of valves) and thus to make the charging of the grid control a larger current. The measurement is then best carried out by compensating the anode current, using a pointer instrument as a null instrument (fig. 13). The range of application of photoelectric cells is continually being extended.

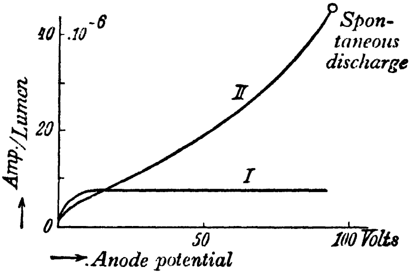

Fig. 12.—Characteristic curves of (I) a vacuum type of photoelectric cell and (II) a gas-filled photoelectric cell.

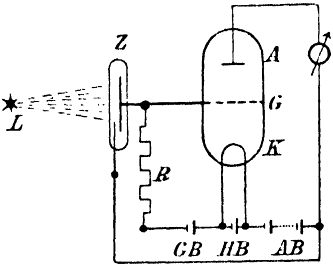

Fig. 13.—Amplifier circuit for photoelectric measurements

L, source of light; Z, photoelectric cell; R, grid leak resistance; A, anode; G, grid; K, cathode; AB, anode battery; HB, filament battery; GB, grid bias battery.

In addition to numerous applications for scientific purposes in the fields of photometry and astronomy, mention may be made of their very extensive use in sound films, picture telegraphy, television, and a great variety of technical relay devices.

2. The Internal Photoelectric Effect

The Primary Current.—A photoelectric effect in the interior of a transparent body can best be detected by the motion of the liberated charges when a field is applied. Thus the effect is manifested by the occurrence of conductivity on illumination, or perhaps an increase of an original " dark " conductivity. The processes involved are extremely complicated. GUDDEN and POHL (1921) were the first to unravel the fundamental process and to demonstrate the migration and replacement of the electrons liberated by the light (the so-called *primary photoelectric current*). They carried out investigations with well-insulating crystals such as diamond, zinc sulphide, and rock salt, and confined themselves to low intensities. In the apparatus shown in fig. 14 the crystal D is clamped between the electrodes K^- and K^+

and illuminated all over. We may suppose that the absorption is approximately uniform throughout. The light liberates electrons from the positively-charged centres in the crystal (see below). These centres remain at rest, but the electrons move under the influence of the applied field. This movement is measured by the electrometer E (so-called negative part of the primary current). In this connexion it is to be remembered that if in a given time n electrons have each moved through an average distance x, then the electrometer indicates the charge fraction nex/d, where d is the distance from K^- to K^+ and e is the electronic charge. On our assumption that the crystal is uniformly illuminated, the fraction x/d cannot exceed the value $\frac{1}{2}$ when averaged over all the electrons. This maximum is reached when (as has been realized in some cases) the electrons are able to traverse the whole crystal and thus all reach the anode. With diamond this can be realized for thicknesses not exceeding 1 mm. In such a case the crystal remains with a positive *volume charge*. If, on the other hand, x is of molecular order of magnitude, a polarization of the crystal remains. The crystal is now in a new physical state: it is " activated " or " excited ". This is manifested by the appearance of a new region of light absorption at the long-wave end of the normal band. The excitation can be destroyed by thermal agitation or by irradiation with light corresponding to the long-wave absorption region, the return to normal being accompanied by the re-entry of electrons or by the redistribution of electrons previously displaced. These charge displacements are observed at the electrometer as the so-called positive part of the primary current.

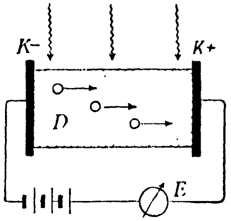

Fig. 14. — Apparatus for measuring the primary photoelectric current.

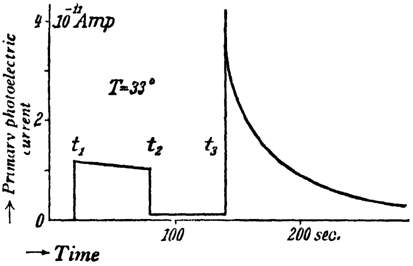

Fig. 15.—Primary current variations in an experiment with NaCl (after Pohl)

Fig. 15 shows the variations of current for a crystal which is a comparatively good insulator. Illumination begins at the time t_1. A current immediately flows, its strength remaining practically constant during the period of illumination. This is the current produced by the migration of the electrons liberated by the photoelectric effect. A slight falling-off is due to a gradually increasing volume polarization and the consequent weakening of the field. At time t_2 illumination ceases. The current falls nearly to zero, all that is observed being the replacement of the migrated electrons as a result of thermal agitation in the circuit. In the present example (NaCl at 33° C.) this is just perceptible. Heating or irradiation with long-wave light (at time t_3) greatly accelerates this replacement. The current strength therefore rises markedly, only to sink gradually to zero as normal conditions are re-established.

Gudden and Pohl also succeeded (1923) in demonstrating the parallelism between the electron displacements and the glow of phosphorescent substances, their after-glow, and the increase of glow produced by heating or irradiation with long-wave light, thus making a considerable advance on Lenard's interpretation of phosphorescence phenomena (p. 174).

As has been shown by Hilsch and Pohl (1929), the photoelectric effect in potassium iodide, for example, does not result directly from the absorption of short-wave light. On the contrary, the immediate result is the formation of absorption centres (concentration about 10^{-6}), which first exhibit the photoelectric effect. These centres give the salt a characteristic absorption spectrum, displaced in the longer wave-length direction relative to that of the normal salt. In silver bromide, for example, the centres correspond exactly to the latent image of photographic plates. According to recent investigations of Pohl and his co-workers, the particular state involved in these long-wave absorptions is mainly characterized by loosely bound electrons. It is possible to introduce such electrons into the crystal in various ways and thus to produce the state associated with long-wave absorption. One way is by making an alkali metal diffuse into the crystal lattice; another is the introduction of electrons from a pointed cathode into the slightly heated crystal; or the electrons may be shot in as rapid cathode rays. Those electrons which are loosely bound in the crystal lattice can then be liberated by light or heat and made to migrate in the crystal under the influence of an electric field. Such a migration can be followed in a very striking manner by the spread of coloration through the crystal (fig. 16).

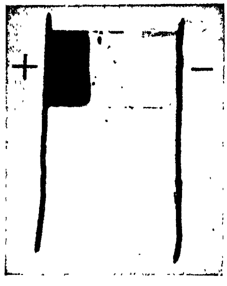

Fig. 16.—Visible migration of a "swarm" of electrons in a KBr-crystal. Natural size. (After Pohl.) Platinum electrodes fused on.

[From *Naturwissenschaften*, 1933 (Springer, Berlin).]

The quantum equivalent law holds very well in the long-wave absorption regions (fig. 17). Here the number of electrons is equal to the number of absorbed light quanta, whereas in the normal absorption region of shorter wave-length the yield is much smaller. Such anomalously small yields indicate the occurrence of absorption processes which are not photoelectrically effective.

Alkali halides coloured by means of neutral alkali atoms show a very marked selective effect (referred to incident light energy). This seems to justify the assumption that the selective surface effect of alkali metal films (p. 124) is due to the absorption spectrum of the atoms adsorbed on the surface.

The Secondary Current.—In addition to the phenomena discussed above, longer intensive illumination produces a current (the so-called *secondary current*) which varies in a complicated way with intensity and previous treatment. An appreciable time is required for this current to attain its full strength or to die away. The effect appears to be due to a diminution of resistance caused by disturbances of the crystal lattice following the extensive liberation of electrons. The applied potential then causes the secondary current to flow through the crystal. The strength of this current may in certain circumstances be much greater than that of the primary current. It is then the only photoelectric effect detected by the less sensitive types of instruments. On account of the very complicated underlying processes, however, the laws of this conductivity change are still very little understood.

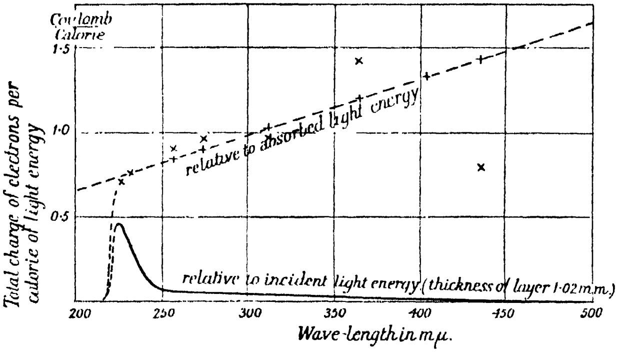

Fig. 17.—Quantum yield in the internal photoelectric effect of diamond × absorption curve from optical measurements. + rounded-off values. (After Gudden and Pohl.)

[From Müller-Pouillet, *Lehrbuch der Physik*, II, 2, II (Vieweg, Brunswick).]

The phenomena become even more complicated when there is an appreciable conductivity even in the dark, i.e. when the application of a potential produces a so-called **dark current** before illumination begins.

In spite of these disadvantages, practical use is made of selenium and thallium sulphide cells, the latter consisting of a melt of thallium sulphide and oxide. They offer the possibility of obtaining comparatively strong currents; and nowadays their disadvantages appear to have been so far overcome as to enable them to be used satisfactorily in practice for sound reproduction.

The Blocking-layer Photoelectric Effect.—In the external photoelectric effect (as, e.g., in fig. 18, Vol. III, p. 312) a current flows even when no voltage is applied. The actual current observed depends on the magnitude and direction of the contact potential differences arising at the electrodes. On the other hand, in the internal photoelectric effect (as, e.g., in fig. 14, p. 129) no current is observed unless a potential difference is applied. Under certain circumstances, however, a current may be produced in the direction of illumination, even without the application of an auxiliary voltage.

As early as 1876 Adams and Day discovered that an appreciable current was produced when a selenium cell was illuminated without a potential being applied. This effect can be well observed with the following apparatus. A piece of wire gauze (see fig. 18) is pressed upon a layer of cuprous oxide (Cu_2O) produced by oxidizing the surface of a massive copper plate by some means or other. The layer of oxide is illuminated through the gauze and a galvanometer is connected between the gauze and the main copper plate. During illumination a current is observed (the direction of flow being indicated in the figure). This arrangement has the further peculiarity that if a potential * is applied in the dark, a current will only flow in one sense, namely that corresponding to passage of electrons from the copper to the cuprous oxide. The interface between the copper and the cuprous oxide forms a so-called **blocking layer.** Arrangements of this kind can be used as dry rectifiers. It can be shown that the electrons liberated in the cuprous oxide pass through the blocking layer, thereby giving rise to the photoelectric current (so-called *blocking-layer photoelectric effect*). On account of the relatively large currents produced (see Table XIII) and the absence of initial inertia, this effect has become of great practical importance. Types of cell in which the light has to penetrate

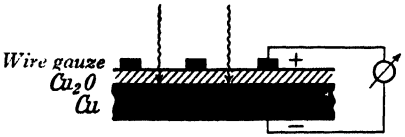

Fig. 18.—Blocking-layer photoelectric effect

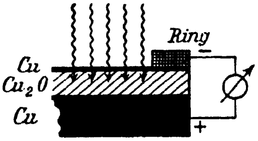

Fig. 19.—Front wall blocking-layer photoelectric cell

Table XIII.—Sensitiveness of Photoelectric Cells

Cell	Photoelectric current in 10^{-13} ampere per lux of incident light energy	
	Without applied potential	With 100 volts applied
Potassium, vacuum type	0·1	3
Potassium, gas-filled type	0·1	86
Blocking-layer type ..	500–5000	—

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* Up to a few volts.

through the cuprous oxide before reaching the blocking layer are known as **back-wall cells.*** Fig. 19 shows a different apparatus, the so-called **front-wall cell,†** which has a thin transparent film of copper deposited upon a more massive cuprous oxide layer. Here the upper blocking layer is effective, since the strong absorption in the oxide prevents the light from reaching the lower oxide-metal interface.

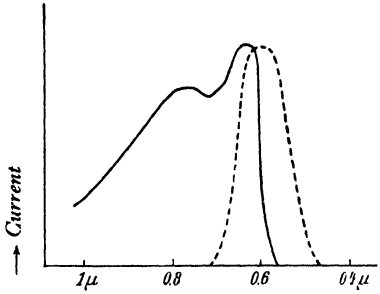

Fig. 20.—Spectral distribution of sensitivity for blocking-layer cells

Continuous curve, cuprous oxide cell referred to uniform spectral distribution of energy. Dotted curve, selenium cell illuminated by tungsten arc (not referred to uniform spectral energy distribution).

Curves of the spectral distribution of sensitivity are shown in fig. 20. Instead of cuprous oxide, amorphous selenium is sometimes used as the sensitive material.

Taking the limit of current detectable by an electrometer as about 10^{-15} ampere, the minimum light intensity which can be detected by a photo-cell turns out as about 3×10^{-15} calories per sec. per sq. cm. Thus the sensitiveness equals that of the eye. By the adoption of certain artifices (working near the conditions for spontaneous discharge) this sensitiveness may be increased about 30 times, or even 10,000 times, if an arrangement similar to a Geiger counter ‡ is used (limit of detection about 2×10^{-19}) cal. per sec. per cm.^{2}).

Blocking-layer photoelectric cells enable light energy to be directly transformed into electrical energy. The yield is too small for practical purposes, but with a good cuprous oxide cell of area 50 sq. cm. it is possible to drive a toy electric motor by ordinary sunlight.

3. The Photoelectric Effect in the X-ray Region

As is shown by fig. 7, p. 111, the intensity of the photoelectric effect increases as the wave-length is made shorter. It is still observed in the X-ray region (compare p. 54).

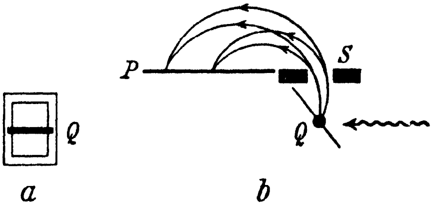

Fig. 21.—Diagram of apparatus for investigating the velocities of photo-electrons by the magnetic deflection method

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* Ger. *Hinterwandzellen.* † Ger. *Vorderwandzelle.*

‡ The mode of action is like that of the Geiger counter (see Vol. III, p. 351), but the point is replaced by a stretched wire.

Velocity of the Photo-electrons.—The velocity of the photo-electrons liberated by X-rays is best investigated by the magnetic method (p. 44), which permits direct photographic recording of the velocity distribution. The cloud-chamber and the retarding potential methods are also applicable.

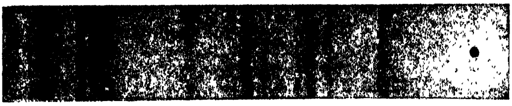

Fig. 22.—Magnetic spectrum of photo-electrons from gold (Incident radiation mainly Mo Kα, $\lambda = 0{\cdot}71$ Å.)
[From *Handbuch der Physik*, Vol. XXIII, 2 (Springer, Berlin).]

Photographic Recording by the Magnetic Method.—Fig. 21 shows the principle of an apparatus for this purpose. The X-rays are incident upon the material at Q, the specimen being in the form of a narrow strip (see the smaller diagram 21*a*). The photo-electrons pass through a slit S and are brought down upon a photographic plate by means of a magnetic field. A linear trace is obtained for each different velocity. The whole apparatus is in a vacuum. By suitable adjustment of the position of the plate it is possible to get a certain focussing effect, electrons of a given velocity but slightly different initial direction being concentrated again into one line on the plate. An example of a record is given in fig. 22. For a discussion of it, see below.

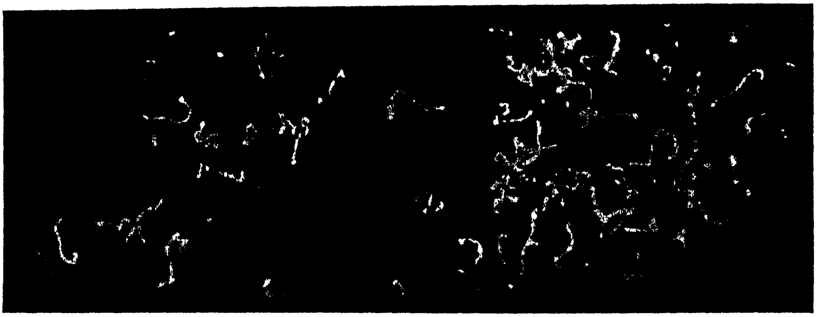

Fig. 23.—Photo-electron tracks in argon, produced by monochromatic X-ray irradiation (Ag-K) (after Kirchner)
[From *Handbuch der Experimentalphysik*, Vol. XXIV, 1 (Akademische Verlagsgesellschaft, Leipzig).]

Direct visual information is given by the cloud-chamber method. Fig. 23 shows a photograph of the photoelectric effect produced by monochromatic X-rays ($\lambda = 0{\cdot}56$ Å.) in argon. We see that the electrons nearly all have the same range and hence, by p. 42, the same initial velocity. This can be deduced directly from stereoscopic photographs. The measurements prove that the equation

$$eU = h\nu - p$$

holds satisfactorily for the velocity of the photo-electrons liberated by X-rays from a solid or a gas.

As regards the value of p, measurements have shown that it is equal to $h\nu_c$, where ν_c is the frequency of the absorption edge of the characteristic radiation of the element in question (p. 78). If ν_i is the frequency of the incident X-rays, we therefore have

$$\tfrac{1}{2}mv^2 = eU = h\nu_i - h\nu_c.$$

For example, the following groups of electrons can be seen in fig. 22, p. 134:

1. $h\nu_i$ — Au L III.
2. $h\nu_i$ — Au M I.
3. $h\nu_i$ — Au M II.
4. $h\nu_i$ — Au M III.
5. $h\nu_i$ — Au M IV + V.
6. $h\nu_i$ — Au N, O.

Thus in these cases the photoelectric phenomenon is to be regarded as the taking up by the atom concerned of a quantity of energy corresponding to the absorption edge of the K, L, or M series, the balance of the energy originally contained in the incident quantum giving the photo-electron its kinetic energy (and negligible potential energy).

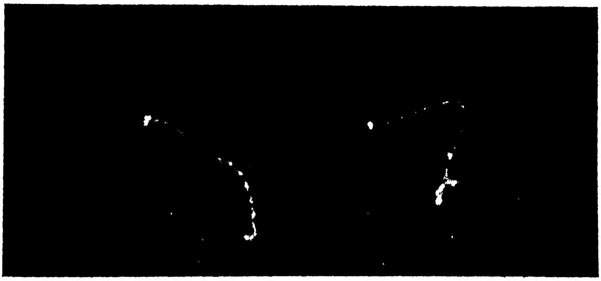

Fig. 24

Figs. 24, 25, 26.—Cloud-track photographs of the ordinary photoelectric emission and the characteristic emission of electrons in krypton under the influence of X-rays of different frequencies. (Fig. 24, 14,000 volts; fig. 25, 20,000 volts; fig. 26, 28,000 volts.)

Auger (1926) was, however, able to show that in certain circumstances the initially-absorbed part of the energy may also reappear as the energy of a photo-electron. In such cases two electrons are expelled simultaneously from the same atom. One of these possesses a quite definite energy determined by the nature of the atom concerned and equal to the energy of an absorption edge. This energy is independent of the frequency of the incident X-rays, provided only that this is high enough to exceed that of an absorption edge of the atom—especially the K-edge. This kind of electron ejection on irradiation is called *characteristic* electron emission. On the other hand, the other electron simultaneously ejected merely has the excess energy $(h\nu_i - h\nu_c)$.

This is well brought out by figs. 24, 25, and 26, which show the photoelectric effect produced in krypton by X-rays of different frequencies (here expressed in terms of the exciting potential). In fig. 24 the incident radiation corresponds mainly to the K absorption edge of krypton (14,000 electron-volts). Hence practically the only electron emission is the characteristic emission (electron tracks about 2 cm. long). There is no energy left over for an ordinary photo-electron. In fig. 25 the X-rays are produced with a potential of 20,000 volts, so that the excess of energy over that of the K-edge is now about 6000 electron-volts. In the middle of the figure we can see the additional track of a photo-electron ejected with this energy. This track appears as a shorter companion to the characteristic electron track of the same length as in fig. 24. In fig. 26 the excess energy of the incident quantum over the energy of the absorption edge is 14,000 electron-volts. Both types of emitted electron now have the same energy. This is clearly evident from the equal lengths of the tracks in each pair.

Fig. 25

Fig. 26

As regards the directional distribution of the photo-electrons, it has been found that (in accordance with the transverse nature of the electric vector of the incident waves) the emission is mainly at right angles to the direction of irradiation, with a certain preference for the forward direction (see fig. 27).

For further details about the *recoil electrons,* which predominate more and more as the incident wave-length is made shorter and which are emitted mainly in the direction of the incident radiation, see pp. 55 and 237.

B. EXCITATION OF LIGHT EMISSION BY COLLISION

4. Emission of Light due to Bombardment with Electrons

The converse of the photoelectric effect is also known, namely, the transference of the kinetic energy of an electron to an atom and the consequent emission of light by the latter. As has already been explained on p. 49, no appreciable energy exchange occurs when electrons with velocities below a certain minimum collide with the atoms of gases which have low electron affinities (p. 53). Accordingly, no emission of light is observed in these cases (see below); for by fundamental energy principles such an emission cannot occur unless that energy is transferred to the gas. The experiments referred to on p. 51 show that such a transference does actually take place at higher electron velocities, and then the gas is caused to emit light, as in the well-known glow of discharge tubes.

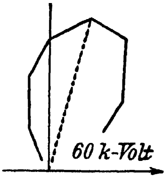

Fig. 27.—Directional distribution of photo-electrons from $CHCl_3$ relative to direction of incident beam (after Bothe).

It has been found that the spectral constitution of the emitted light varies with the amount of energy transferred. This follows in particular from observations of LENARD and STARK on the emission from flames and arcs as well as from discharges in gases. A further discussion of these results will follow later (p. 221). Both observers found a marked variation of the spectral constitution of the emitted light with the energy of excitation. GEHRKE and SEELIGER (1912) were the first to investigate more closely the emission of light due to excitation by electrons of definite velocities. They obtained the important result that *no emission* occurs below a certain electron velocity. This shows that in the excitation the deciding factor is the energy of each individual electron and that as a rule a deficiency in this individual energy cannot be compensated by the accumulated energies of larger numbers of electrons. This is the analogue of LENARD'S result for the photoelectric effect, namely, that the intensity of the light has no effect on the energy of the photo-electrons. RAU (1914) was further able to show that different electron velocities are necessary for the excitation of different spectrum lines in He—e.g. within a series (p. 182) the lines of shorter wave-length appear at higher electron velocities. The quantitative relationship was first established by FRANCK and HERTZ in 1914. They found that at the minimum electron velocity (4·9 volts) at which energy is transferred to the atoms in mercury vapour, the light emitted proves on spectral examination to be monochromatic (wave-length 2537 Å., frequency $1{\cdot}183 \times 10^{15}$ sec.$^{-1}$). In the experimental investigation it is necessary to exclude the possibility of multiple collisions occurring to an appreciable extent, i.e. an atom which has already taken up energy from an electron must not be allowed to collide with another electron. This can be done by using the least possible concentration of gas and electrons.

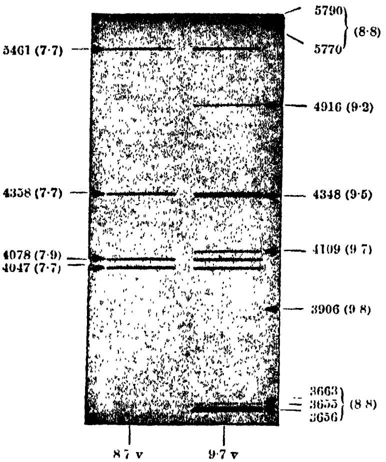

Fig. 28.—Spectra showing that bombarding electrons must possess a certain minimum energy in order to excite lines.

[From H. Hertz, *Zeitschrift f. Physik*, 1924.]

Fig. 28 shows the changes which occur in the emission spectrum of mercury as the electron energy is increased. We see that this increase in energy causes the appearance of more and more lines, some of longer wave-length and some of shorter wave-length than those already excited.

The great significance of these experiments lies in the following remarkable relationship. The energy of the incident electron (4·9 volts) is found to be equal (within the limits of error) to $h\nu$, where ν is the frequency of the emitted spectrum line (2537 Å.) and h is the constant (Planck's quantum of action $6{\cdot}55 \times 10^{-27}$ erg sec.). Thus we have

$$eU = h\nu.$$

In our particular case: $6{\cdot}55 \times 10^{-27}$ (erg sec.) $\times$ $1{\cdot}18 \times 10^{15}$ (sec.$^{-1}$) $= 7{\cdot}75 \times 10^{-12}$ erg, and $1{\cdot}59 \times 10^{-19}$ (coulomb) $\times$ 4·9 (volts) $= 7{\cdot}8 \times 10^{-19}$ (watt-sec.) $= 7{\cdot}8 \times 10^{-12}$ erg.

This relationship has been found to hold for a number of spectral lines, which (for a reason to be discussed later (p. 155)) are called **resonance lines.** An energy of *at least* $eU = h\nu$ is required to excite the emission of a spectral line of frequency ν.

As can be seen from fig. 28, however, it does not follow that every line of frequency ν appears when the energy $h\nu$ is transferred to the atom. This happens only for the resonance lines; for the remaining lines a greater energy is necessary. Thus, e.g., the new lines appearing in the right-hand spectrum of fig. 28 require an electron energy of over 9 volts, although their $h\nu$ values are actually much smaller than that of the resonance line of higher frequency which is excited at 4·9 volts. This curious behaviour is of fundamental importance for our knowledge of the connexion between the energy changes of atoms accompanying emission of light. The more detailed discussion which follows on p. 176 will bring out the simple relationships involved.

Mention may be made here of a method, applied by Franck and Einsporn, in which the appearance of new lines in the ultra-violet during the excitation of mercury vapour by electrons is detected by means of the photoelectric effect produced in an auxiliary iron electrode. As the electron velocity is gradually increased, sudden discontinuities occur in this photoelectric effect. These are due to sudden increases of photoelectric current resulting from increases in the ultra-violet intensity (in general caused by the appearance of new emission lines of mercury (see fig. 36, p. 52)). It has been found that the potentials at which these new lines appear bear a close relationship to the energy states of the mercury atom.

The Excitation Function.—The number of collisions of an electron with a gas molecule under given conditions can be calculated from the kinetic theory. Hence, by measuring the electron current and the amount of light produced, it is possible to evaluate the fraction of the collisions which are fruitful in exciting emission. Measurements of this kind carried out by Hanle and Schaffernicht give the result that only a few per cent of the calculated gas-kinetic collisions actually lead to emission. The yield varies very much with the velocity of the electrons used. The form of the function (the so-called *excitation function*) is as shown in fig. 29.

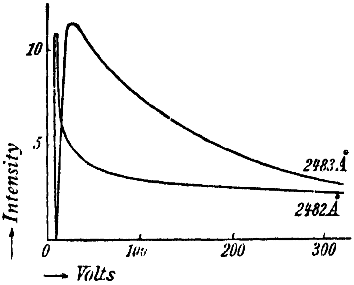

Fig. 29.—Excitation functions for two mercury lines (after Schaffernicht)

C. Temperature Radiation

5. Radiation Equilibrium

The emission of light may occur as a consequence, not only of the impact of electrons, but also of collisions with other atoms or molecules. This is shown very clearly by the glow of the rapidly flying atoms in canal or positive rays (Vol. III, p. 340), and especially by the emission of light from bodies at high temperatures. In the latter case the statistical distribution of the atomic or molecular energies (Vol. II, p. 40) gives rise to special regularities, which have proved to have a decisive bearing on the theory of light emission. We shall therefore proceed to discuss them in greater detail.

Coefficients of Reflection, Absorption, and Transmission.—When radiant energy falls on a body, it is in general divided up into three parts: one part is reflected at the surface of the body, the second penetrates into the interior of the body and is absorbed there, while the third is transmitted by the body. If we call these three parts respectively R, A, and T and take the total incident energy as unity, we must have

$$R + A + T = 1.$$

R is called the coefficient of reflection, A the coefficient of absorption, and T the coefficient of transmission of the body. The actual values depend on the substance in question and the physical condition of the surface, as well as upon the wave-length of the incident radiation.

For polished metals the *coefficient of reflection* is in general very high. Thus, e.g., it may be as high as 0·98 for polished silver mirrors, i.e. 98 per cent of the total incident energy may under certain circumstances be reflected back. The coefficient of transmission of metals is very low: metals, even in relatively thin layers, are practically opaque to all wave-lengths. Bodies which are transparent in the usual sense of the word have a high *coefficient of transmission* for the visible region of the spectrum. They may, however, be quite opaque to certain non-visible regions. For example, many kinds of glass in layers of 1 cm. thickness let through up to 70 per cent of all normally incident radiant energy of visible wave-lengths, but are almost entirely opaque for the ultra-violet and the infra-red. The *coefficient of absorption* in the visible region is high for all dark-coloured bodies. Thus even a very thin layer of lamp-black absorbs practically the whole of the visible light incident upon it.

We can imagine a body which absorbs the *whole* of the radiant energy falling upon it, reflecting none and transmitting none. Such a body would necessarily appear *black*, both by reflection and by transmission. Such a body, which absorbs all the radiant energy which falls on it, may be referred to as a **perfectly-black body.**

The absorption of radiation means that the energy incident upon the body in question is transformed into internal heat energy. This must cause a rise in the temperature of the absorbing body, which may be used to measure the quantity of energy absorbed.

By taking as black an absorbing body as possible, the quantity of *incident* energy can be measured in this way. A blackened thermometer or a suitable thermo-element may be used.

Radiation Equilibrium.—If the temperature of a body exceeds that of its surroundings, a process of temperature equalization sets in spontaneously. When the body is surrounded by material substances, the processes of convection (motion of large quantities of matter) and conduction (transmission of energy from molecule to molecule) play important parts. The process of temperature equalization persists, however, even when the body is placed in a perfect vacuum and is supported in such a way that conduction is negligible. The rate of equalization of temperature depends, other things being equal, upon the size of the body and the nature of its surface (see p. 151, also

Vol. II, p. 179). The transference of energy is brought about by electromagnetic waves. These usually have a relatively long wave-length; only when the temperature is very high do they extend into the visible region. Such an equalization of temperature is said to take place by **heat radiation.**

Let us imagine that the radiating body, which for the sake of simplicity we take to be spherical and homogeneous, is enclosed in an evacuated space bounded on all sides by a shell made of a substance opaque to the radiation. Then the electromagnetic waves passing out from the body must strike the shell and give up their energy to it either wholly or partially, i.e. the shell is heated up. At the same time the shell radiates its heat into the interior in the form of electromagnetic waves, some of which fall on the body. After a certain time has elapsed the body will have attained the same temperature as the shell, and from that point onwards the quantity of energy radiated (**emitted**) by the body in unit time will remain equal to the quantity received and taken up (**absorbed**) by it in unit time from the shell.

No matter what the material of the body or the physical state of its surface, the temperature equilibrium is determined by the fact that the quantity of radiant energy emitted by the body in unit time is equal to the amount absorbed by it in unit time. Thus temperature equilibrium is to be regarded not as a static condition, but as one involving a dynamic exchange of energy between the body and its surroundings.*

If the body in the enclosure is perfectly-black in the sense defined above, it will absorb the whole of the radiant energy incident upon it and will transform this radiant energy into thermal energy of its own atoms and molecules. If we take the total quantity of incident radiation as unity, we see that the coefficients of reflection R and transmission T are zero, while the coefficient of absorption A is unity.

The *quantity* of radiant energy emitted by the body per unit time (its *intensity of emission*) depends on its temperature. It is also different for different wave-length regions. Hence the quantity of energy absorbed per unit of time must also depend on the same factors; for in the case under discussion it is equal to the quantity emitted in unit time.

Let us now imagine the perfectly-black body replaced by some other body, e.g. a sphere with a coloured surface. This new body absorbs only a definite fraction of the energy incident upon it. Suppose that its coefficient of absorption is a, where $a < 1$. Then since this body also assumes a constant temperature when placed in the enclosure, it follows that at equilibrium the quantities of energy emitted and absorbed in a given time must again be equal. This must be true for every wave-length, i.e. *in radiation equilibrium a body emits precisely the same radiation as it absorbs.*

---

* This view was first put forward by C. Prévost (1787–1855), a French geologist. It is often referred to as Prévost's *theory of exchanges.*

This is only true on the assumption that the whole of the energy absorbed by the body is transformed into kinetic vibrational energy of its molecules, i.e. into thermal energy, and that the source of the radiation emitted by the body is this inherent thermal energy of its molecules. Radiation for which this is the case will be referred to in future as **temperature radiation.** If any part of the absorbed energy is transformed into some other form of energy, or if the emitted radiation has its source in some form other than heat (e.g. if chemical energy plays a part in either process), then the above considerations are no longer valid.

6. Kirchhoff's Law of Emission and Absorption

Consider a perfectly-black body at the centre of an evacuated enclosure bounded by perfectly-black walls. Let heat energy be supplied continuously to the body and removed continuously from the walls of the enclosure, so that in spite of their mutual exchange of energy by radiation their respective temperatures T and T_0 remain constant. We may imagine, for example, that there is a spiral of platinum wire heated by an electric current in the interior of the body, while the whole enclosure is surrounded by a water-bath at constant temperature.

The temperature T of the body at the centre of the enclosure being higher than T_0, that of the walls, the quantity of energy radiated by the body and absorbed by the walls of the enclosure must be greater than that radiated from the walls and absorbed by the body in the same time. Let $E d\lambda$ be the quantity of energy emitted by the body in unit time in the wave-length region between λ and $\lambda + d\lambda$ and A its coefficient of absorption. Then $E/A = F$ is a function of λ, the wave-length emitted, and the temperatures T and T_0. We may accordingly write

$$\frac{E}{A} = F(\lambda, T, T_0).$$

In the case of a perfectly-black body the whole of the incident radiation is absorbed; thus we have $A = 1$, and the equation takes the simpler form

$$E = F(\lambda, T, T_0).$$

We may simplify it still further by supposing the temperature of the walls of the enclosure to be the absolute zero. Then

$$E = F(\lambda, T).$$

We now imagine the black body replaced by some other body which absorbs only a fraction of the radiant energy incident upon it. Everything else we leave as before, arranging that the temperature of the body is maintained at T and that of the container at the absolute zero. If e is the quantity of energy emitted per unit of time, and a the coefficient of absorption, we have

$$\frac{e}{a}=f(\lambda, \mathrm{T}).$$

Similarly, for any other body we have

$$\frac{e_1}{a_1}=f_1(\lambda, \mathrm{T}).$$

Kirchhoff showed theoretically in 1859 and 1862 that the functions f and f_1 must be identical with one another, and hence also identical with F for the perfectly-black body.

This is **Kirchhoff's law** of the emission and absorption of temperature radiation:

$$\frac{e}{a}=\frac{e_1}{a_1}=\mathrm{E}.$$

In words: *The ratio of the amount of energy radiated per unit of time to the fraction of the incident energy absorbed is the same function of the wave-length and the absolute temperature for all bodies, and is equal to the amount of energy radiated in unit time by a perfectly-black body under the same conditions.*

Kirchhoff's law depends on the second fundamental law of thermodynamics. It may be easily proved in a particular case. Imagine two plates, made of substances with respective intensities of emission e and e_1 (as above) and coefficients of absorption a and a_1, so placed that all the radiation sent out by the one plate is incident upon the other. If the temperature is initially the same for both, then by the second law of thermodynamics this equality of temperature must persist; neither plate can become heated up at the expense of the other. Now in unit time the first plate radiates a quantity e of energy to the second, which absorbs the fraction a_1e and reflects back the rest $e(1-a_1)$. This reflected part again falls on the first plate, which absorbs the fraction $e(1-a_1)a$ and reflects the residue $e(1-a_1)(1-a)$. This last part again falls on the second plate, and the processes of partial reflection and partial absorption are repeated. The total quantity of energy radiated from the first plate to the second and absorbed by the second in these processes is therefore

$$ea_1+ea_1(1-a_1)(1-a)+ea_1(1-a_1)^2(1-a)^2+\ldots=\frac{ea_1}{1-(1-a_1)(1-a)}.$$

Again, the second plate radiates the quantity e_1 of energy to the first, which similarly absorbs the quantity

$$\frac{e_1a}{1-(1-a_1)(1-a)}.$$

The quantity reflected by the first plate is therefore

$$e_1-\frac{e_1a}{1-(1-a_1)(1-a)};$$

and this must be the quantity of its own radiation which is absorbed by the second plate in the backward and forward reflection process. The total amount absorbed by the second plate is therefore

$$\frac{ea_1}{1-(1-a)(1-a_1)}+e_1-\frac{e_1a}{1-(1-a)(1-a_1)}.$$

Now in order that the temperature of the plate may remain constant, the quantities of energy absorbed and emitted must be equal. Therefore

$$\frac{ea_1}{1-(1-a)(1-a_1)}-\frac{e_1a}{1-(1-a)(1-a_1)}+e_1=e_1,$$

whence

$$ea_1=e_1a$$

or

$$\frac{e}{a}=\frac{e_1}{a_1}.$$

Deductions.—We transform the above equation by writing

$$e(\lambda, \mathrm{T})=a(\lambda, \mathrm{T})\mathrm{E}(\lambda, \mathrm{T}).$$

Since $a(\lambda, \mathrm{T})$ is certainly less than unity, it follows that:

The intensity of emission from a perfectly-black body is greater than that from any other body.

Hence if we determine the values of E for any body and plot them against the wave-length, the curve obtained must lie entirely within the corresponding curve for a perfectly-black body.

Again, we may write the equation in the transposed form

$$a(\lambda, \mathrm{T})=e(\lambda, \mathrm{T})/\mathrm{E}(\lambda, \mathrm{T}).$$

If we confine our attention to one particular wave-length, this reduces to

$$a(\mathrm{T})=e(\mathrm{T})/\mathrm{E}(\mathrm{T}),$$

from which it follows that to every finite value of a which is not zero there must correspond a finite value of e which is not zero. The case $\mathrm{E}=0$ is excluded, because the intensity of emission of a perfectly-black body is always greater than that of any other body; and the case $\mathrm{E}=\infty$ is also excluded, because with a finite supply of heat the rate of emission can never become infinite. We therefore make the following deduction:

In pure temperature radiation every body absorbs those wave-lengths which it emits at the temperature in question.

7. The Law of Black-body Radiation

Even the simplest observations (say upon an incandescent lamp lit by different currents) show that with increase of temperature there is an increase in the rate of emission of radiation and at the same time a change of colour in the direction of less redness or greater blueness.

A great deal of effort has been expended, both from the experimental and the theoretical side, in formulating the laws underlying these changes. It may be remarked in advance that these laws only apply to radiation into a vacuum. If the radiator is surrounded by a medium of refractive index n, it is necessary (as KIRCHHOFF has shown) to introduce the factor n^2.

The Stefan-Boltzmann Law.—STEFAN * was the first to succeed in formulating a law (1878). This was later (1884) deduced theoretically by BOLTZMANN † and recognized as applicable to perfectly-black bodies only. The Stefan-Boltzmann law is as follows:

The total rate of radiation from a perfectly-black body is proportional to the fourth power of the absolute temperature. Thus at the absolute temperature T each unit of area of the surface of a perfectly-black body radiates towards one side (into a solid angle of 2π) in each second the total energy S, which is given by the equation

$$S = \sigma T^4,$$

where σ is a constant.

The accurate observations of LUMMER and PRINGSHEIM (1897) and KURLBAUM (1898) showed that this law is actually in complete agreement with the best experimental data for a perfectly-black body. With a possible error of a few per cent, $\sigma = 5{\cdot}77 \times 10^{-5}$ erg cm.$^{-2}$ sec.$^{-1}$ degree^{-4} = $5{\cdot}77 \times 10^{-12}$ watt cm.$^{-2}$ degree^{-4} = $1{\cdot}378 \times 10^{-12}$ cal. cm.$^{-2}$ sec.$^{-1}$ degree^{-4}.

Realization of the Perfectly-black Body.—We consider a space entirely bounded by walls which are all at the same temperature and all impervious to radiation. KIRCHHOFF pointed out that every beam of radiation within such a hollow enclosure must be identical with that which would be emitted by a perfectly-black body at the same temperature. Thus the radiation of the enclosure is independent of the nature and shape of the bodies bounding it and is determined solely by the temperature. Hence the radiation of an ideal black body can be imitated to any desired degree of approximation by utilizing a constant-temperature enclosure with a small hole through which a beam of radiation can emerge.

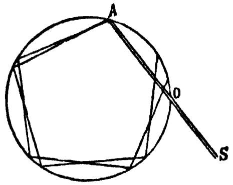

Fig. 30.—Path of a beam of light in an enclosure

Fig. 30 represents such an enclosure, which may be made, e.g., of metal coated inside with some good absorbing material such as lamp-black, platinum black, or the like. The small aperture is at O. We now consider a beam of radiation from outside which passes in through this aperture. It falls on the inner side of the wall at A and is there to a large extent absorbed. A certain fraction, however, is reflected and strikes the inner side of the wall again. Here a further large fraction is absorbed, but some is again reflected, only to strike the inner side of the wall farther on. Thus the beam is many times reflected before any fraction of it can reach the opening again; and by then this fraction is so small as to be negligible. Thus the enclosure acts as a perfect absorber, i.e. as a perfectly-black body.

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* J. STEFAN (1835–1893), Professor of Physics at Vienna.

† LUDWIG BOLTZMANN (1844–1906), one of the founders of the kinetic theory of gases. He was a professor of theoretical physics, notably at Vienna.

The difference between the blackness of such a chamber and the ordinary blackness of a blackened surface can be well seen by painting a cigar box inside and out with black paint and then making a hole in the side of the otherwise completely closed box. The hole looks much blacker than the outer surface.

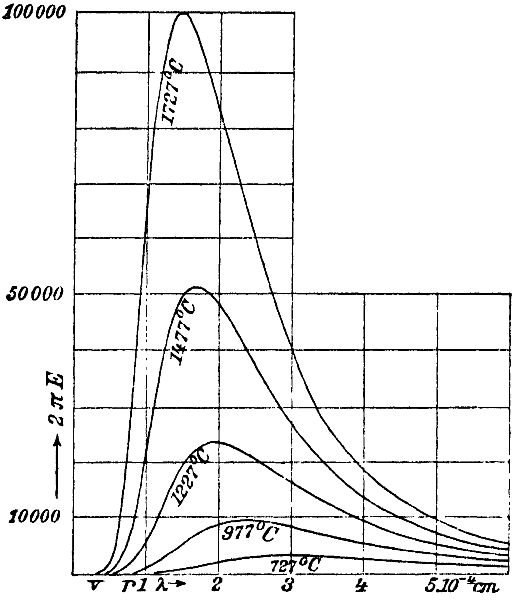

Fig. 31.—Radiation isothermals for a perfectly-black body

In order to realize a perfectly-black body **Lummer** and **Pringsheim** used double-walled vessels, keeping the space between the walls at constant temperature by filling it with steam, ice, liquid air, or some other substance. For higher temperatures they used an internally-blackened porcelain tube heated in an electric furnace, or alternatively a tube made of carbon which could be heated directly up to 2300° C. by passing an electric current through its walls. In all their experiments they found the **Stefan-Boltzmann** law to be in complete agreement with observation.

In all radiation measurements it must be remembered that the receiver is emitting radiation as well as the original radiator. Hence the temperature of the receiver must also be known and the corresponding radiation subtracted from that which is to be measured. For example, if the original radiator has the absolute temperature T and the receiver has the absolute temperature T′, then in applying the **Stefan-Boltzmann** law we must write

$$S = \sigma(T^4 - T'^4).$$

Results of Investigations on Perfectly-black Bodies.—There are two ways in which we may investigate the relationship between temperature and intensity of emission over the wave-length region from λ to $(\lambda + d\lambda)$. The first is to keep the temperature of the radiator constant and to determine the value of E for each wave-length in turn. This gives the so-called *radiation isothermal*—see figs. 31 and 32—for the temperature in question. Alternatively we may confine our attention to one wave-length and make a series of measurements for different temperatures. This gives a so-called *isochromatic curve*—see fig. 33.

The area included beneath any particular isothermal of fig. 31 represents the total intensity of emission S. We see that this increases very rapidly with rise of temperature, in accordance with the Stefan-Boltzmann law. We see further that the maximum is displaced towards shorter wave-lengths with rise of temperature.

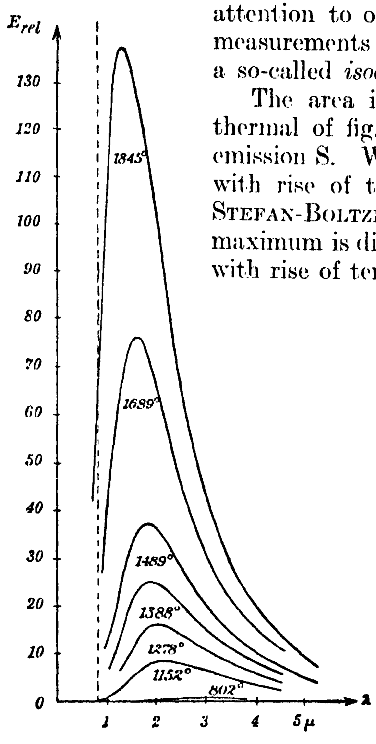

Fig. 32.—Radiation isothermals for incandescent platinum

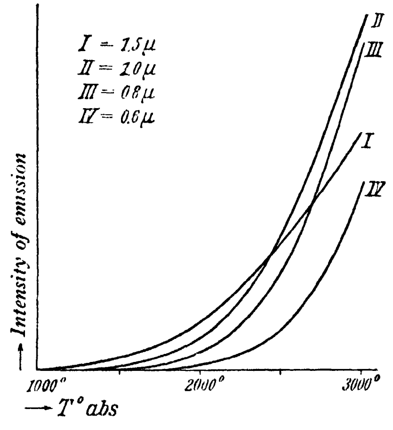

Fig. 33.—Isochromatic curves for a perfectly-black body

The theoretical explanation of the relationships expressed in fig. 31 presented very great difficulties, the origin of which is now known to lie in the inapplicability of so-called classical electrodynamics (i.e. the theory of Faraday and Maxwell, which holds for macroscopic fields) to the processes of emission and absorption of light. From the historical point of view it is of great interest to note that it was Planck's theoretical treatment of black-body radiation (1900) which led to the discovery of a quantitative theory of the special phenomena which arise in the interaction of matter and radiation.

Wien's Displacement Law.—In 1893 W. Wien * succeeded in obtaining an important partial solution of the problem on the basis of classical theory. He deduced that *the wave-length of maximum intensity of emission* E *of a black body is inversely proportional to the absolute temperature.*

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* Wilhelm Wien (1864–1928), professor at Würzburg and (from 1920 onwards) at Munich, received the Nobel Prize in 1911.

We may write this

$$\lambda_{\max} T = \text{constant} = 0{\cdot}2884 \text{ cm. degree}$$
$$= 2884\mu \text{ degree.}$$

Thus, as is shown in fig. 31, the maximum is displaced in the direction of shorter wave-length with rise of temperature. It first comes into the visible region at about 3800° abs., for which $\lambda_{\max} = 760 m\mu$.

The intensity of emission at the maximum can be obtained by combining the STEFAN-BOLTZMANN law with WIEN's displacement law. This gives

$$E_{\max} = \text{constant} \times T^5$$
$$= 2{\cdot}08 \times 10^{-5} T^5 \text{ erg cm.}^{-3} \text{ sec.}^{-1}$$
$$= 0{\cdot}497 \times 10^{-12} T^5 \text{ cal. cm.}^{-3} \text{ sec.}^{-1}.$$

Thus whereas the total intensity of emission S increases with the fourth power of the temperature, the intensity $E_{\max}$ at the maximum of the isothermal curve increases with the fifth power of the temperature. There is also a simultaneous shift of the maximum towards shorter wave-lengths.

Planck's Radiation Law.—In 1900 PLANCK found the following analytical expression for the quantity of energy $E_\lambda d\lambda$ radiated per second from unit area of the surface of a black body (i.e. into the solid angle 2π):

$$E_\lambda d\lambda = c_1 \frac{\lambda^{-5}}{e^{c_2/\lambda T} - 1} \cdot d\lambda.$$

Here $E_\lambda d\lambda$ is that part of the total radiation which corresponds to wave-lengths between λ and $\lambda + d\lambda$. The constant c_1 has the value $5{\cdot}88 \times 10^{-6}$ erg cm.^{2} sec.$^{-1}$ = $0{\cdot}140 \times 10^{-12}$ cal. cm.^{2} sec.$^{-1}$ for plane polarized light. For ordinary light (the case usually observed) the value is twice as great. The value of c_2 is 1·43 cm. degree.

Both the STEFAN-BOLTZMANN law and the WIEN displacement law can be derived immediately from PLANCK's expression, the former by integration ($S = \int E_\lambda d\lambda$) and the latter from the condition that E_λ shall be a maximum.

The term -1 in the denominator of PLANCK's formula can be neglected when λT is small (in the visible region up to about 3000°). The equation thus obtained had previously been deduced by WIEN on the classical theory. It is, as we see, a limiting case of PLANCK's equation, which covers *all* cases. The simplified equation may also be written in the form $\log_e E_\lambda = a - (b/T)$. Fig. 34 shows a graph of results obtained by LUMMER. The linear relationship between log E and the reciprocal of T, required by the theory, is satisfactorily fulfilled. Such lines are called logarithmic isochromatic curves.

The theoretical derivation of PLANCK's radiation formula shows that the constants c_1 and c_2 bear simple relationships to other natural constants. The train of thought underlying the proof is somewhat as follows. According to classical views, the emission of an electromagnetic wave is due to the non-uniform motion of electric charges (Vol. III, p. 622). If we take the simplest case of one positive charge and one negative charge (forming a dipole (Vol. III, p. 99)), an oscillation of these charges relative to one another will give rise to the emission of an electromagnetic wave of the same frequency. Now atoms may be regarded as systems capable of performing such oscillations—so-called oscillators; for in consequence of their masses and the electrical forces holding them together they have a certain natural frequency associated with them. The amplitude and frequency of the oscillations, however, are functions of the temperature. If we confine our attention to pure temperature radiation (i.e. if we exclude all other sources of energy), the whole of the energy emitted by the atomic oscillators must be derived from their thermal motions. Similarly, all the radiation they absorb is eventually transformed into thermal energy. Since the oscillators are able to transform radiation into heat and vice versa, a certain state of equilibrium will be attained when radiation and matter are allowed to interact. Radiation in equilibrium with any perfectly-black body is called **black-body radiation.** In such radiation the energy is distributed in quite a definite way throughout the spectrum, or (in other words) amongst the different frequencies ν. For the radiation of frequency ν_1 is in equilibrium with oscillators of frequency ν_1; these in turn are in equilibrium with other oscillators of frequency ν_2 through the electric fields in the interior of the matter, and these finally are in equilibrium with radiation of frequency ν_2. Hence there must be a perfectly definite equilibrium between the radiations of frequencies ν_1 and ν_2.

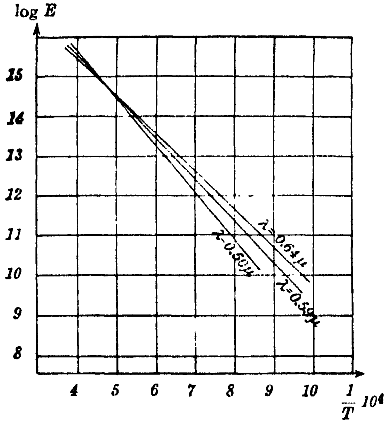

Fig. 34.—Logarithmic isochromatic curves for the visible region

According to the theorem of the equipartition of energy which we have previously mentioned in Vol. II, p. 40 and repeatedly used, the thermal energy (in thermodynamical equilibrium) must be equally distributed among all the mutually-independent parameters of state of which the energy is a quadratic function. The frequencies of the oscillators and the radiation are obviously parameters of this description (Vol. II, p. 44); for two oscillations of different frequencies are quite independent of one another and the radiation of the one frequency cannot be directly transformed into radiation of the other frequency. Radiation of one particular frequency interacts only with oscillators of the same frequency. Hence according to the theorem of the equipartition of energy we should expect the mean energy of each oscillator to be the same, and also the mean energy of each " individual radiation " present in the black-body radiation to be the same. Of course this assumes that we have solved the problem of how a definite number of parameters are to be ascribed to the radiation as a number of oscillators are ascribed to the body. An energy distribution of the above kind is the inevitable deduction from the **Maxwell-Boltzmann** theorem of "classical" thermodynamics. Now there can be no doubt that in actual fact this theorem is inapplicable. For the number of oscillators of independent frequencies in a perfectly-black body, like the number of the frequencies themselves, has no upper limit. Again, the number of different "individual radiations" is unlimited. A given quantity of energy cannot be *equally* distributed in a finite manner among this infinite array of different "individual radiations" and their parameters. If the theorem of equipartition of energy were actually valid without restriction for oscillatory processes in nature, then it can be shown that at thermodynamical equilibrium all thermal energy would necessarily be transformed into radiation energy, or that if thermodynamical equilibrium were established between the different "individual radiations", all the energy would pass over to the greatest frequencies, i.e. be absorbed into the extreme ultra-violet. In any spectrum, therefore, we should expect to find most of the energy at the extreme short-wave end. All this, however, is contrary to experience. The "classical" theorem of the equipartition of energy cannot therefore hold without restriction for oscillatory processes; in fact, restrictions must be made in the case of high frequencies.

M. **Planck** showed that agreement with experiment is obtained if the following assumption is made: *the energy of an oscillator must be an integral multiple of the quantity* hν, *where* ν *is the frequency and* h *a universal constant equal to* $6{\cdot}547 \times 10^{-27}$ erg sec. According to this assumption, the energy of the oscillators is not continuously distributable, but only in certain minimum quanta of energy. This is analogous to the fact that the mass of matter is not continuous in character, but consists of minimum quanta of mass—the atoms.*

The content of the above quantum hypothesis seems to represent a fundamental property of atoms, due to the nature of the interaction between nucleus and extra-nuclear electrons. It contradicts the fundamental concepts of "classical" physics which had proved so successful in explaining phenomena involving bodies of macroscopic size. Thus the energy of ordinary acoustic oscillators (or any macroscopic oscillators) is for all practical purposes continuously distributable. We can see at once, however, the extent of the restriction imposed by **Planck**'s quantum hypothesis upon the theorem of equipartition of energy. Since the value of h is so extremely small, the product $h\nu$ must also be small. The quantum hypothesis states that the energy of an oscillator cannot change by an amount less than $h\nu$. Now if ν is sufficiently small, the value of $h\nu$ will be so extremely small that the energy changes will still be practically continuous in character, as is required in classical physics. The hypothesis therefore does not appreciably affect oscillators of low frequency. But as we pass to greater and greater frequencies, the value of $h\nu$ will increase progressively, until eventually it is actually greater than the mean thermal energy of a gas molecule or of an oscillator at the temperature in question. Under these conditions an oscillator of such a frequency will only be able to take up energy from another molecule in those comparatively rare cases where the energy of the molecule happens to exceed the value $h\nu$. Thus the higher the value of ν, the less will the oscillator contribute to the radiation; and from a certain frequency upwards no radiation will be observable. Rise of temperature (i.e. increase of the mean energy of the colliding molecules) must displace the radiation spectrum towards higher frequencies, as is actually observed.

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* It is interesting to note that **Boltzmann** had previously (1877) considered this possibility. He writes: "Let each molecule be capable of taking up only a finite number of kinetic energy values (*lebendige Kräfte*). For further simplicity let us assume that these kinetic energy values which can be taken up by each molecule form an arithmetical progression, e.g. $0, \epsilon, 2\epsilon, 3\epsilon, \ldots, p\epsilon$."

The assumption that an oscillator can only possess integral multiples of a certain energy quantum (from which we deduce, for example, that a certain minimum energy is necessary to excite the oscillator) has proved extremely fruitful. The modifications required in certain circumstances will be dealt with later. Special importance attaches to the quantum hypothesis in connexion with the new views on the interaction of matter and radiation to which it gave rise. Since the energy of the oscillators can only change by whole quanta, the radiant energy may also be regarded as made up of these units, i.e. as localized in discrete *light quanta*. This one theory has proved capable of providing simple and satisfactory explanations of a number of previously inexplicable phenomena, such as the photoelectric effect, the excitation of light emission from atoms by bombardment with electrons, and the short-wave limit of white X-rays (see above, p. 53).

From what has been said above it will be clear that the constants in PLANCK'S radiation equation (p. 148) must be expressible in terms of the universal constants $h = 6{\cdot}547 \times 10^{27}$ erg sec. (known as **Planck's quantum of action,** since erg sec. is the unit of action—see Vol. I, p. 91), $c = 3 \times 10^{10}$ cm. sec.$^{-1}$ (the velocity of light, which comes in because the radiation is electromagnetic in character), and finally $k = 1{\cdot}37 \times 10^{-16}$ erg degree^{-1} (BOLTZMANN'S constant, which is characteristic of the thermal motion of matter—see Vol. II, p. 60). Actually it can be shown that $c_1 = c^2h$ and $c_2 = ch/k$. Hence it follows that $\sigma = 2\pi^5k^4/(15c^2h^3)$. The values calculated from the theory are in good agreement with experiment.

The experimental measurement of σ and of the constants of WIEN'S displacement law provides two equations from which h and k can be determined. Since further $k = R/n$ (Vol. II, pp. 40, 41), a value of Avogadro's constant can be obtained from measurements of temperature radiation, i.e. by a purely optical method. The calculation, first made by PLANCK in 1901, gives a value in good agreement with the results obtained by quite different methods (see Vol. II, p. 60).

8. Non-black Bodies. Temperature Measurement and Light Sources

Behaviour of Non-black Bodies.—All the actual substances available to us have absorption coefficients a less than unity. If the absorption coefficient is the same for all wave-lengths, the body is called a **grey radiator** (arc-lamp carbon, $a \sim 0{\cdot}8$; carbon filament, $a \sim 0{\cdot}7$). If a varies with the wave-length, the body is said to show **selective radiation.** This is accordingly characterized by the fact that the body absorbs less (and consequently emits less) than a perfectly-black body, at least over certain regions of wave-length. For an example see fig. 35.

In order that a grey or selective radiator of temperature T may give the same total intensity of emission S as a perfectly-black body of temperature T_b, it follows that T must be greater than T_b. We may call T_b the **black-body temperature** of the actual radiator. With platinum at the melting-point, for instance, the difference $T - T_b$ is 210°. The black-body temperature of the crater of a carbon arc is 3500°, whereas the true temperature is about 4000°. For practical purposes it is the curve of sensitiveness of the eye which is the decisive factor in judging radiation (see Vol. IV, p. 31). We may give the name **colour temperature** to that temperature which a perfectly-black body would have to possess in order to appear to the normal eye the same colour as the radiator in question. For grey radiators the colour temperature is the same as the true temperature; it is only the surface intensity which is less than for a black body. One result of the spectral distribution of sensitiveness of the human eye is that the observed brightness of an emitter increases very rapidly with rise of temperature from the point at which the glow first becomes visible (for a completely-rested eye about 400° C.—the so-called grey glow; feeble red glow, about 630° C.). Thus LUMMER and PRINGSHEIM found that the brightness, as judged by the eye, increased in proportion to the thirtieth power of the absolute temperature in the region of red heat and to the twelfth power even in the region of white heat.

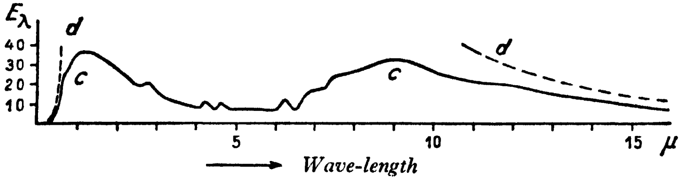

Fig. 35.—Spectral distribution of the radiation from a Welsbach mantle (*c*) and that from a perfectly-black body (*d*) at the same temperature

[From Gehlhoff, *Lehrbuch der technischen Physik*, Vol. II (Barth, Leipzig).]

Pyrometry.*—Because of these marked changes of brightness the temperature of a glowing body can be measured very accurately by photometric methods. Instruments used for this purpose are called **optical pyrometers.**

The action of the much-used pyrometer of HOLBORN and KURLBAUM, for example, is as follows. The surface under investigation is viewed through an electric lamp bulb and the current passing through the lamp is adjusted until the filament is observed to disappear, owing to its brightness becoming just equal to that which is to be measured. The lamp is calibrated against a black body at known temperatures obtained by using suitable substances of known melting-points. If the brightness to be measured is too great, it is first weakened by the interposition of suitable absorbing glass screens or filters. Optical pyrometers calibrated as above give black-body temperatures directly.

Sources of Light.—Most of the sources of light in common use to-day are temperature radiators. In candle and paraffin-oil flames the glowing bodies are the solid carbon particles derived from the burning gases; in incandescent lamps the glowing part is the metal filament, in arc lamps (with pure carbons) mainly the positive crater (see Vol. III, p. 352). In the last-mentioned case, however, electrically-excited emission of the gases in the arc also occurs, so that such sources (especially arcs using cored carbons containing volatile salts) cannot be regarded as pure temperature radiators. As was shown in Vol. IV, fig. 20, p. 31, the amount of energy in the visible region is only a small fraction of the total electromagnetic energy emitted (compare fig. 32, p. 147). For practical purposes, too, the spectral curve of sensitiveness of the eye is of great importance. Owing to the form of this curve (Vol. IV, fig. 19, p. 31), a definite quantity of energy in the green-yellow region of the spectrum produces a more intense sensation than the same quantity in the red or blue regions. As we see from fig. 31, p. 146, the fraction of the total radiation lying in the visible region increases with rise of temperature, the visually-estimated intensity increasing (as we mentioned above) proportionally to the twelfth power of T. This explains why attempts are made to increase the temperature of light sources as far as possible. The historical development of electric lighting has been based on this (see Vol. III, p. 258).

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* Gr. *pyr*, fire.

Theoretically an optimum point would be reached as the temperature was progressively raised. This would occur when, in accordance with Wien's displacement law, the maximum intensity of emission had been brought to coincide with the spectral region to which the eye is most sensitive. For a perfectly-black body this optimum temperature lies at about 6000–7000° abs., the corresponding emission being 81 lumens per watt (see Vol. IV, p. 22). If the temperature is raised still further, the fraction of the emitted radiation which is useful for visual purposes falls off again, more and more energy passing over into the shorter-wave (ultra-violet) regions of the spectrum. Table XIV gives the optical and visual efficiencies of the total emission of a black body at different temperatures. By optical efficiency we mean the percentage of the total energy emitted which lies in the visible region ($4 \cdot 1$–$7 \cdot 2 \times 10^{-5}$ cm.), and by visual efficiency the percentage obtained by multiplying the optical efficiency at the wave-length in question by a factor which is a measure of the sensitiveness of the eye in that region. Thus monochromatic radiation with the wave-length corresponding to the maximum sensitiveness of the eye ($\lambda = 555 m\mu$) would have a visual efficiency of 100 per cent. The corresponding emission is 697 lumens per watt.

Table XIV

Temperature, Deg. Absolute	Efficiency	
	Optical ( )	Visual ( )
1,000	$3 \cdot 33 \times 10^{-4}$	$2 \cdot 43 \times 10^{-5}$
2,000	1·00	$2 \cdot 46 \times 10^{-1}$
3,000	9·30	3·11
4,000	22·8	8·11
5,500	36·0	13·0
6,000	38·9	13·9
7,000	39·0	13·8
8,000	38·2	13·1
10,000	31·0	10·6

We see that even in the most favourable case of an ideal temperature radiator (i.e. a perfectly-black body) at the optimum temperature of 6000–7000° abs.

only about 14 per cent of the theoretical energy can be utilized. In actual practice, however, the limit is less than 5 per cent.

The visual efficiency can be improved slightly by using selective radiators. Naturally we choose those which, although they emit a smaller total amount of energy at any given temperature than a black body, have a specially high emission in the visible region of the spectrum (fig. 35, p. 152). Such selective emission can be realized particularly well by renouncing temperature radiation as a source of light and using emission due to other causes (e.g. bombardment by electrons accelerated in electric fields) which do not depend upon the statistical distribution of thermal energy.

The spectrum of electrically-excited radiation from gases is in general discontinuous. Up to a short time ago it was necessary to use high potentials, on account of the large cathode fall (Vol. III, p. 334). This was an obstacle to the general use of such illumination, and these light sources were therefore only used for advertisements and for special purposes (e.g. CO_2 discharges were used in dye-works, &c., on account of the similarity of this light to ordinary daylight). Now that the use of incandescent cathodes has been found to reduce the cathode fall to a relatively low figure (see Vol. III, p. 334), gas discharge tubes can be lit directly from the mains, and their more extensive use in the future is extremely probable. Already some main streets are illuminated by sodium lamps.

The emission of the CO_2 lamp (without incandescent cathode) is only 3–5 lumens per watt, but for neon and mercury lamps the figure has been raised to 35 and for sodium to 50. The surface brightness can also be increased by narrowing down the path of the discharge (see Table XV; compare Vol. IV, Table I, p. 25).

Table XV.—Surface Brightness of Light Sources used in Practice

Source of Light	Diameter of Tube in cm.	Current Density in amp./sq. cm.	Surface-brightness in Candle-power/sq. cm.
Acetylene flame	—	—	up to 9·0
Carbon filament lamp	—	—	71
40-watt vacuum tungsten lamp ..	—	—	238
100-watt gas-filled tungsten lamp	—	—	800
2000-watt gas-filled tungsten lamp	—	—	1900
Positive crater, carbon arc ..	—	—	15.000
Moore lamp (CO_2)	4·0	0·025	0·2
Neon advertising tube	2·0	0·025	0·25
Neon tube with incandescent cathode (100 amp.)	6·5	3·0	15
Constricted neon discharge ..	0·2 (diaphragm)	800	600 (axial)

On account of their descending characteristic (Vol. III, p. 354) these tubes with incandescent cathodes must be used with a resistance or a condenser. This causes an energy loss of about 50 per cent or about 10–15 per cent respectively.

D. FLUORESCENCE AND PHOSPHORESCENCE

9. Fluorescence of Gases

Above we have considered the excitation of light emission from atoms or molecules by transference of energy from moving electrons. There is another means of excitation—by light. Atoms and molecules are able to take up light of certain frequencies, and this absorbed energy may under certain circumstances be emitted again wholly or partially. When the re-emission follows immediately upon the absorption (p. 165), it is called **fluorescence.** When, on the other hand, there is a relatively long time-lag between the two processes (in certain cases even years), the phenomenon is called **phosphorescence.** An alternative classification, which is practically identical with the above but refers rather to the elementary processes involved, defines the re-emission as fluorescence when it is from the atom which absorbed the energy, and as phosphorescence (found mostly with very complicated molecules) when it occurs after some intermediate process (see below) and at some place different from the place of absorption. We will first consider the simplest cases, which occur in gases.

Resonance Radiation.—The fundamentally simplest case is that in which an atom of a gas absorbs monochromatic light and then re-emits light of the same frequency.

This is analogous to the mechanical case of resonance. If two tuning-forks of the same frequency are set up and one is made to sound, then the second is also set vibrating and itself becomes a source of sound emission. The energy emitted by the second fork is derived from that sent out by the first (exciting) fork, and is re-emitted after absorption (see Vol. II, p. 197). A similar effect is observed if we press down the loud pedal of a piano and then sing a note into the instrument. The particular string which happens to be in resonance with the note sung gives a marked response.

This phenomenon was first observed in the optical region by R. W. Wood in the case of sodium vapour. The light of a bunsen flame coloured with sodium and hence emitting the D lines (Vol. IV, p. 158) is concentrated upon a well-evacuated vessel containing a piece of pure sodium and heated to about 100° C. A yellow glow is seen in the vessel in the path of the incident beam. The sodium vapour in the vessel (the pressure at this temperature should be about 10^{-7} mm. of mercury) lights up under the influence of the incident light, and the re-emitted spectrum can be shown by spectroscopic examination to consist of the D lines again. This sort of emission is called **resonance radiation,** and the emitted spectrum lines are called **resonance lines.** If the vapour pressure of the sodium in the vessel is increased by raising the temperature, the surface brightness of the effect is increased but the glow no longer extends so far into the interior of the vapour. A relatively small depth of the now denser gas is able to absorb the incident light completely. At about 300° C. (the sodium vapour being still saturated) the whole of the glow is confined to a very thin surface layer at the point of incidence of the beam. The *volume resonance* has given place to *surface resonance.* It is easy to show that under these conditions practically all the incident light is re-emitted. This can be done by covering a portion of the area of incidence with MgO (by combustion of Mg), which provides a very white scattering surface. The MgO is observed to have the same brightness as the surface layer of gas. The yield by resonance is therefore 100 per cent.

This yield, however, is not obtained unless the bunsen used as the source of the exciting light contains only a small concentration of sodium (i.e. is only feebly coloured). The reason is as follows. In the vessel the sodium vapour is at a relatively low temperature and hence at a very low pressure, so that the thermal motions and mutual interaction of the atoms are slight. In the bunsen flame, on the contrary, the sodium vapour is at a high temperature and (if much salt is introduced) at a relatively high concentration. Both these circumstances result in strong interactions between the atoms by collision, and consequently the emitted radiation is spread out over an appreciable spectral range. A definite broadening of the D lines is observed in the spectroscope. The high temperature has another effect tending in the same direction, in that the Doppler effect (p. 219) is increased when the thermal motions become more energetic. The relatively cold and rarefied gas in the resonance vessel possesses a very sharp absorption (half-value width,* about 0·02 Å. at 300° C.) and hence can absorb only the central portion of the broadened line incident upon it. The remainder of the incident light, namely, that with frequencies differing slightly from the absorption frequency of the vapour, passes through unabsorbed, like any other light, and is ineffective as far as the excitation of resonance is concerned. Hence in order to make the resonance effect as intense as possible, it is necessary to use special lamps (usually low-voltage discharge tubes containing rare gases) which give very narrow (i.e. very nearly monochromatic) lines.

Similar phenomena to those described above for Na are also observed for Li (6708 Å.), K (7699 and 7645 Å.), Ag (3382 and 3280 Å.), and Hg (2536·7 and 1849 Å.), as well as for Cd, Zn, and Ca. For a great many purposes it is convenient to use mercury, since in this case the phenomena are well developed at room temperature; but mercury has the disadvantage that the resonance radiation lies in the ultra-violet and so can only be investigated photographically. In order to excite the resonance radiation of mercury it is necessary to use well-cooled mercury lamps in which the discharge is made to occur close to the wall. Otherwise the middle portion of the resonance line emitted in the inner regions of the lamp is absorbed in the lamp itself by the cooler mercury vapour nearer the wall. This process is called *self-reversal.*

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* The half-value width is the difference between the wave-lengths of the two points on the absorption curve (one on each side of the maximum) at which the intensity is half the maximum intensity.

Successive Excitation.—The following experiment (FÜCHTBAUER, WOOD) is very informative in connexion with the behaviour of atoms taking up radiant energy. A vessel R containing mercury vapour (fig. 36) is irradiated by means of a mercury resonance lamp Hg R, all light of wave-length longer than 3000 Å. being stopped by a suitable filter F. Investigation by means of a quartz spectrograph with its slit placed at S shows that the mercury vapour in R emits the resonance line 2537 Å. The resonance lamp is then switched off and R is irradiated with the light from the ordinary uncooled mercury lamp Hg II, which does not emit any resonance line, since the latter is absorbed in the lamp itself. This self-reversal is indicated in the figure by the filter F, which is supposed to absorb all the resonance wave-length emitted by Hg II. Spectrographic examination of the vapour in R then shows that it is not emitting appreciably at all. If now the resonance lamp Hg R is brought into action (i.e. if the vessel R is irradiated by both lamps at once), it is found that the spectrum emitted by the vapour in R contains not only the resonance line but also a considerable number of other lines in the ultra-violet and visible regions. The explanation of this behaviour is as follows. The mercury atom which absorbs radiation of the resonance frequency thereby passes out of its **ground state** (i.e. the stable state of minimum energy) into a state of higher energy, a so-called **excited state.** The observed phenomena can be explained very easily on the view that such excited atoms possess a characteristic absorption spectrum different from that of atoms in the ground state, i.e. that excited atoms are able to absorb other mercury lines besides the resonance line. These absorptions cause the excited atoms to pass over into states of still higher energy, from which they then revert to the ground state with emission of light. This view has stood all tests and will be discussed in greater detail below (p. 176). In some cases, e.g. the rare gases, it has been found possible to demonstrate directly the characteristic absorption spectra of excited atoms of the kind postulated here .

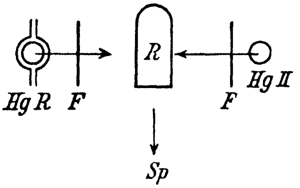

Fig. 36.—Diagram of apparatus for demonstrating successive excitation

General Fluorescence of Gases.—The conditions are not always so simple as in the case above. For example, in many metal vapours (i.e. in monatomic gases) absorption causes a glow whose spectrum contains, apart from the absorbed wave-length, one or more additional lines of somewhat longer wave-length, which in general do not occur as absorption lines. This occurs, for instance, with Tl, Pb, Bi, and Sb. An interpretation has again been found possible on the basis of the structure of the atom concerned (p. 180).

Still more complicated spectra are obtained when molecules containing more than one atom (e.g. iodine, I_2) are excited so as to emit light. When the concentrated beam from an arc lamp is passed through a well-evacuated, sealed glass globe containing a few fragments of iodine, the vapour is seen to give a very intense yellowish-green fluorescence. The emitted light, when examined by a spectrograph, is found to consist of a large number of spectrum lines lying close together (see fig. 37). The phenomenon is simplified by irradiation with monochromatic light. The fluorescence spectrum then contains the exciting line and also a number of new lines arranged in a regularly-spaced sequence on the long-wave side—the so-called **resonance spectrum** (fig. 37). If the iodine vapour is raised to a higher temperature, lines are also obtained on the short-wave side of the exciting line, with the same regular spacing.

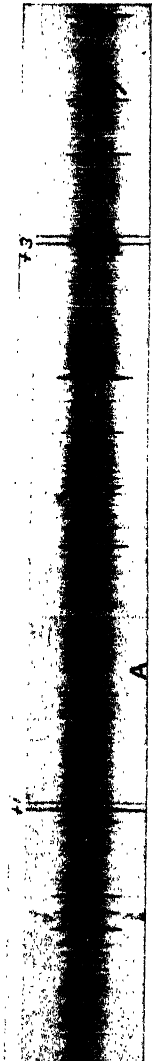

Fig. 37.—Spectrum of the fluorescence of iodine vapour: numbers 0 to 3 of the resonance spectrum excited by the line 5461 Å.: below, the band spectrum excited by white light

[From Pringsheim, *Fluoreszenz und Phosphoreszenz* (Springer, Berlin).]

Stokes's Rule.—The following observation was made by Stokes * and stated by him in the form of a rule now known by his name:

In almost all fluorescence and phosphorescence phenomena the emitted light is of longer wave-length than (or at least of the same wave-length as) the exciting light, provided that the temperature is not too high.

This cannot be understood on the basis of classical electrodynamics, and remained for fifty years unexplained, i.e. unrelated to other phenomena—the first warning that the classical electromagnetic theory of light would have to be fundamentally modified. Not until the advent of the quantum theory was a satisfactory theoretical explanation forthcoming (see p. 122).

In many instances spectrum lines are emitted in phosphorescence and fluorescence which are of shorter wave-length than the exciting line. Such lines are referred to as *anti-Stokes lines*, which is perhaps not a very happy choice of name. These occasional deviations from Stokes's rule, however, are confined to the appearance of a relatively small number of lines in a relatively narrow region on the short-wave side of the exciting line.

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* **George Gabriel Stokes (1819–1903), Professor of Mathematics at Cambridge from 1849 onwards.**

10. Interaction between Excited and Unexcited Molecules in a Gas

Influence of Additions of Foreign Gases upon the Fluorescence of a Gas.—The fluorescence of a gas is in general affected by the addition of a foreign gas (WOOD, 1911). In all probability the effect, which may be either intensification or weakening of the fluorescence, arises from a number of different causes.

In the first place, there is a change in the conditions of absorption of the exciting light. We must assume that for an atom at rest and unaffected by other atoms the breadth of the absorption line (or emission line) is of the order of 10^{-4} Å. (see p. 219). Thermal motion causes a Doppler effect (Vol. II, p. 280) and consequent broadening of the line, the breadth increasing as the temperature is raised (p. 220). The electric and magnetic fields of neighbouring atoms and molecules also cause a broadening (p. 221).

It is this latter effect which is of importance in the case of admixed foreign gases. Suppose that the exciting source gives a comparatively broad line, e.g. in the case of mercury suppose that a mercury-arc lamp at high temperature and high pressure is used. Further, suppose that the pure gas to be excited is at room temperature and at most at the corresponding very low saturated vapour pressure. It will then absorb only the central portion of the line emitted by the lamp —the very portion that is much weakened by self-reversal in the lamp itself (see p. 156). Under these circumstances addition of a foreign gas, by causing a broadening of the absorption line of the gas under investigation, increases the amount of absorption of the exciting light and thus intensifies the fluorescence. A fourfold increase of intensity was actually observed by WOOD in the case of mercury vapour (resonance line) on addition of helium. The width of the lines is, of course, correspondingly greater than in the pure gas.

If the above effect is avoided by using a narrow sharp exciting line (e.g. from a resonance lamp), then a decrease in the intensity of the resonance radiation is observed when foreign gases are added. The extent of this decrease depends on the chemical character of the added gas and on its concentration. In the case of mercury resonance the least effective gases are the rare gases and nitrogen, the most effective being carbon dioxide, oxygen, and hydrogen.

Increase of the pressure of the fluorescing gas has an effect similar to that produced by admixture of foreign gases. These results indicate that excited gas atoms may collide with foreign molecules (or with other atoms of the fluorescing gas itself) before re-emitting the energy which they have absorbed. As is shown by experiments described below (p. 160), the energy of excitation may be partially or completely transferred to the other atom or molecule taking part in the collision. The energy may thereby be transformed into kinetic energy, in which case the two colliding particles fly apart with increased velocities (the centre of gravity of the pair remaining fixed); or it may be transformed partly into internal energy of the particle struck by the originally excited atom. We shall see below that examples of both kinds of energy transference are known.

It is possible to determine the time during which an atom remains in its excited state, and the number of collisions per second can be calculated from the kinetic theory of gases. Hence we can deduce the fraction of the collisions which take place with an energy transference of the kind referred to above. A difficulty is encountered, however, in connexion with the values to be used for the radii of the atoms concerned. In order to obtain agreement with other observations of the duration of the excited state, it is found necessary to take the effective radius of the excited mercury atom in collisions (compare the effective cross-section, p. 44) as about 1·5 times greater than the radius of the normal mercury atom as obtained from gas-kinetic data. Moreover, the exact value varies with the nature of the added foreign gas. This means that, in consequence of the different strengths of the fields surrounding different atoms, energy transference in collision becomes possible at different distances of approach. The large diminution of intensity of fluorescence caused by hydrogen has a special cause, which will be considered in greater detail later (p. 169).

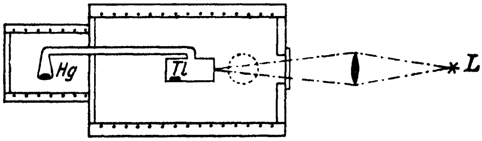

Fig. 38.—Experimental apparatus for demonstrating sensitized fluorescence
[From *Zeitschrift fur Physik*, 1922.]

Collisions of the Second Kind.—We have seen that collisions between atoms or molecules may be inelastic if one of the particles concerned was originally in an excited state. In such cases there is an exchange or transformation of the energy of excitation.

This is in a certain sense the reverse of the process in which atoms or molecules are excited by the impact of other atoms or electrons, i.e. in which the kinetic energy of one of the particles involved in the collision is transformed wholly or partially into energy of excitation.

Inelastic collisions, in which energy of excitation is transformed wholly or partially into kinetic energy, are called *collisions of the second kind.*

Sensitized Fluorescence.—The following is a typical example of a group of phenomena in which energy transferences of the kind considered above play a part.

Two quartz vessels, each heated in a separate electric furnace, are connected by a quartz tube (see fig. 38). One vessel contains metallic thallium and is heated to about 800° C. (when the vapour pressure of thallium is about 2 mm.). The other contains mercury and is heated to about 100° C. Except for these metals the apparatus is well evacuated. The light from a mercury lamp L is focussed on the vapour in the cooler part of the apparatus, and by spectrographic investigation it is found that the part of the illuminated vapour lying close to the wall of the vessel emits, in addition to the mercury resonance line 2537 Å., the thallium lines 2768, 3529, 3776, and 5350 Å. (cf. fig. 39). The effect is confined to the region near the wall of the vessel as a result of the relatively high pressure of the mercury vapour. If the resonance line is filtered out of the incident exciting beam by means of a glass plate, then all the thallium lines vanish. These thallium lines also fail to appear if the mercury vapour is removed from the vessel by freezing out.

This emission by the thallium as a result of excitation of the mercury is called *sensitized fluorescence*, since it is not caused directly by the incident light but through the agency of the excited mercury atoms. The name is chosen by analogy with the sensitization of photographic plates for long-wave rays by means of dyes which absorb the incident energy and then pass it on to the photographic substance (p. 169).

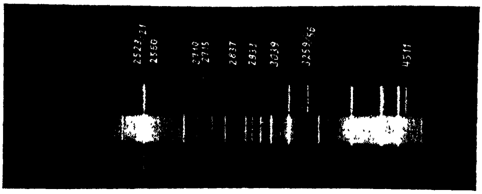

Fig. 39.—Spectrum of the sensitized fluorescence of indium (after Donat). Upper and middle spectrum: mercury lamp (feebly and strongly illuminated). Lower spectrum: mercury spectrum together with the strong fluorescence lines of indium. The exciting line is 2537 Å.

[From *Handbuch der Physik*, Vol. XXIII, 1 (Springer, Berlin).]

The explanation of sensitized fluorescence is as follows. We consider two kinds of atoms A and B with respective energies of excitation $h\nu_A$ and $h\nu_B$. We suppose further that $\nu_B < \nu_A$. When the gas A is irradiated with light of frequency ν_A, we get resonance fluorescence. When the gas B is irradiated with light of frequency ν_A, we get no result, because the gas B will not in general absorb the frequency ν_A. When, however, a mixture of A and B is irradiated with light of frequency ν_A, we get excited atoms of A which may collide with atoms of B and transfer to them a certain part of their energy of excitation. In this way atoms of B become excited and can then emit their own characteristic frequencies. Thus both A and B are found to fluoresce.

Since an atom B only takes up the energy $h\nu_B$ in becoming excited by the impact of an excited atom of A, there is a certain energy balance $h\nu_A - h\nu_B$. This is transformed into kinetic energy of the colliding atoms. We may calculate the resultant velocities by applying the principles of the conservation of energy and of the position of the centre of mass. The initial velocities due to thermal motions may be neglected, since under the experimental conditions considered here they are small (of the order of a tenth of a volt) in comparison with the velocities resulting from collisions of the second kind. We have

$$h\nu_A - h\nu_B = \tfrac{1}{2}m_A v_A^2 + \tfrac{1}{2}m_B v_B^2$$

and

$$m_A v_A = m_B v_B.$$

Hence

$$\tfrac{1}{2}m_A v_A^2 = (h\nu_A - h\nu_B)\frac{m_B}{m_A + m_B}$$

and

$$\tfrac{1}{2}m_B v_B^2 = (h\nu_A - h\nu_B)\frac{m_A}{m_A + m_B}.$$

Thus the greater the difference between the excitation energies of A and B, the greater is the velocity imparted to the atom B as a result of the collision. The velocity of B can be determined from the Doppler effect and the line-breadth which depends on it.

The above conclusions can be tested in the case of thallium and mercury described above. The thallium line 2768 appears only feebly, but the line 3776 is intense. Both are resonance lines of thallium (p. 180). For the line 2768 the difference $h\nu_{Hg} - h\nu_{Tl}$ is only $6{\cdot}4 \times 10^{-13}$ erg, which is of the same order as the energy of the thermal motions of thallium under the conditions of the experiment. Thus the line emitted will be only very slightly broadened by the Doppler effect and will therefore be strongly absorbed (self-reversal) in the thallium vapour itself. This explains why its observed intensity is so low. For the line 3776, on the other hand, the corresponding difference of excitation energy $h\nu_{Hg} - h\nu_{Tl}$ is $2{\cdot}6 \times 10^{-12}$ erg. As the above calculation shows, the velocity imparted to a thallium atom by a collision of the second kind with an excited mercury atom is here very great. The emitted line is therefore much broadened by the Doppler effect and consequently only its central portion is absorbed by the thallium atoms in the remainder of the vapour, which have a much lower average velocity. All of the broadened line except the central portion passes out and is accessible to observation. This explains the large observed intensity.

Various observations, notably upon mixtures of sodium and mercury under excitation by mercury lines (Webb and Wang, 1929) indicate that the probability of transference of excitation energy by collision becomes especially high when $h\nu_B$ is not very different from $h\nu_A$, i.e. when the energy of excitation of the one particle can be transformed almost completely into the energy of excitation of the other. This is reminiscent of the excitation function for electron impact (see fig. 29, p. 139), where the probability of energy transference falls off as eU becomes more and more different from $h\nu$.

A special case of collisions of the second kind is the collision of an ion (which is an atom in a higher excited state) with a neutral atom or molecule. If the latter has a lower ionization potential than the ion which strikes it, it may be ionized by the collision. Here again the probability of this process increases as the difference between the ionization potentials of the two particles becomes less. Examples of reactions actually observed are:

$$He^+ \, (24{\cdot}5 \text{ volts}) + Ne \, (21{\cdot}5 \text{ volts}) \rightarrow He + Ne^+$$

and

$$He^+ + N_2 \, (24 \text{ volts}) \rightarrow He + N_2^+.$$

The figures in brackets are the ionization potentials.

11. Fluorescence of Solids and Liquids

Fluorescence is not confined to gases. A large number of liquids and solids exhibit fluorescence, in some cases very intense fluorescence, when illuminated by suitable light—usually short-wave visible or ultra-violet light. One difference as compared with simple gas fluorescence is that in almost all cases excitation can be effected by relatively broad spectral regions and that the emitted light is likewise spread out over broad spectral bands. Moreover, the fluorescence of liquids and solids is usually confined much more rigidly to the long-wave side of the exciting radiation, i.e. Stokes's rule is more accurately obeyed. Both these differences are probably due to the fact that in solids and liquids the atoms are relatively close together, so that for this reason, as well as owing to thermal motion, the absorbing and emitting atoms are very much distorted as compared with free gaseous atoms. By lowering the temperature, relatively sharp spectra can be obtained in many cases.

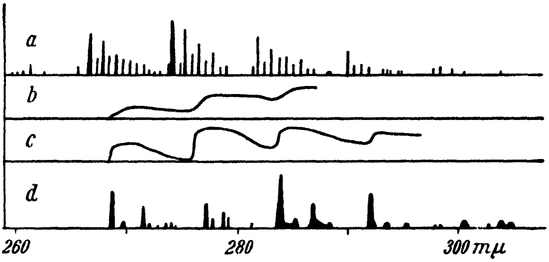

Fig. 40.—Fluorescence of benzene: (*a*) gas, (*b*) liquid, (*c*) solid at 0° C., and (*d*) solid at − 180° C.

Among pure liquids the aromatic hydrocarbons, such as benzene, naphthalene, and anthracene, and many of their derivatives, show the most marked fluorescence. Sometimes the effect is confined to the ultra-violet (e.g. benzene). The substances of not too complicated structure also exhibit fluorescence in the solid state. Fig. 40 shows, for example, the spectra of benzene in the three states of aggregation.

Among pure inorganic solids we may mention the uranyl salts (compounds containing the group UO_2), the salts of the rare earth metals (fig. 41), and calcium tungstate (scheelite) as showing particularly strong fluorescence. There are also many fluorescent systems consisting of very small quantities (fractions of one per cent) of foreign substances, mostly coloured, contained in a colourless main substance. An example is *fluor spar*, from which the phenomenon of fluorescence takes its name. In addition to the immediate fluorescence emission, however, these systems exhibit a persistent after-glow. They will therefore be discussed in the next section; for it has been found that complicated processes, different from simple fluorescence, occur in these systems between the absorption of energy and re-emission of light.

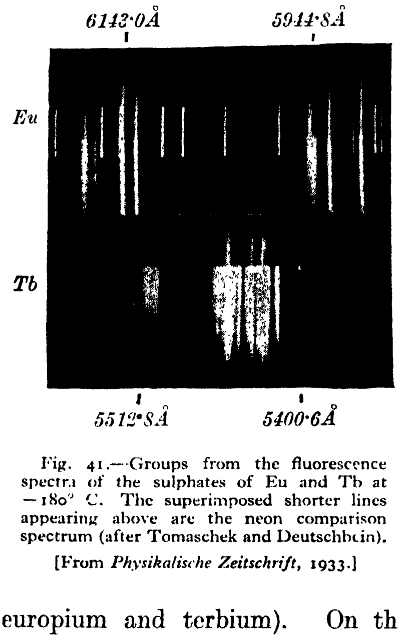

Fig. 41.—Groups from the fluorescence spectra of the sulphates of Eu and Tb at −180° C. The superimposed shorter lines appearing above are the neon comparison spectrum (after Tomaschek and Deutschbein).

[From *Physikalische Zeitschrift*, 1933.]

Ruby, which consists of a solid solution of trivalent chromium in Al_2O_3, exhibits a peculiar behaviour analogous to *resonance radiation* in gases. Two of the strongest lines in its fluorescence spectrum, which lies in the red region, can be excited by light of their own wave-length. Accordingly these lines occur strongly in absorption.

In *solution* (particularly aqueous solution) the only inorganic substances which fluoresce with any notable intensity are the uranyl salts and the salts of some of the rare earths (especially europium and terbium). On the other hand, a large number of organic substances, mostly of complicated structure, are known to fluoresce strongly in solution.

Beautiful fluorescence is exhibited by a solution of quinine in sulphuric acid and also by solutions of many coal-tar dyes, such as *eosin*. The most beautiful is a dilute alkaline solution of *fluorescein*, a substance which owes its name to this property.

When a few drops of an alkaline solution of fluorescein are allowed to fall into a vessel of water through which a beam of light is passing, they are seen to spread out in characteristic brilliant green clouds. A convergent beam of sunlight from a condensing lens, when passed through water containing only a trace of the sodium derivative of fluorescein, produces a luminous green cone. Spectral analysis of the light emitted proves that the effect is not due to simple reflection or absorption. The solution appears reddish-yellow when viewed by transmitted light —a sign that it absorbs the blue end of the spectrum more than the red. If blue and violet light is allowed to fall on the solution, it will be practically all absorbed, provided that the correct concentration is used. But the solution gives a green glow, even although the exciting light contains no green at all. Red light produces no fluorescence. Thus fluorescein has the property of transforming short-wave visible light into longer-wave visible light. This is a good example of Stokes's rule.

The fluorescence spectra of substances in solution consist of diffuse bands (fig. 42), the position of which depends on the nature of the solvent (probably on its dielectric constant). The presence of foreign substances in the solutions produces remarkably large alterations of intensity– usually a decrease, but sometimes an increase. This is reminiscent of the effects of admixture in the case of gases. The mechanism is probably similar to that in gases, the energy of excitation of the molecules of the fluorescent substance being transferred to the foreign molecules by collision and hence being lost so far as fluorescence is concerned.

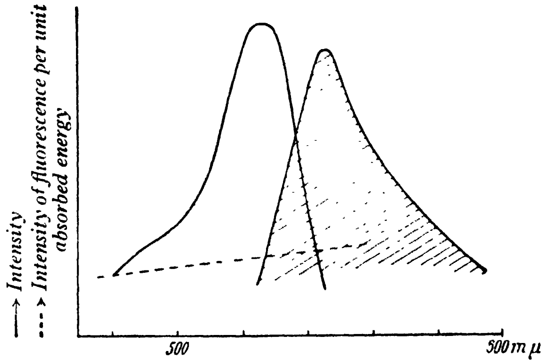

Fig. 42.—Emission band (shaded) and absorption band of eosin in aqueous solution. The dotted line shows the distribution of excitation referred to equal absorbed energies (after Nichols and Merrit).

Above a certain limiting value (usually low), increase of the concentration of the fluorescent solute also diminishes the fluorescence yield, i.e. the quantity of light emitted per unit energy absorbed.

As regards the relation between molecular structure and fluorescent properties, a large quantity of data has been accumulated for organic substances, and it is now possible to state the contribution of different groups and to predict the spectral position of the fluorescence to which they give rise.

Duration of Excited States.—Numerous measurements have been made of the time which elapses between the excitation of an atom or molecule by light absorption and the re-emission of the energy as fluorescence. Gases, liquids, and solids have been investigated. The determinations may be made either with a suitable combination of Kerr cells actuated by very rapid electrical oscillations (Vol. IV, p. 257), or by illuminating one small area of a molecular beam (Vol. II, p. 53) and observing how far the glow extends in the direction of motion of the molecules. Results obtained by these and other methods show that the duration of the excited state is of the order of 10^{-8} second.

12. Energy Transferences involving Excited Atoms and Molecules

Chemiluminescence.—The energy set free in chemical reactions can in many cases give rise directly to emission of light, instead of indirectly by way of temperature radiation. This occurs especially with processes having large heats of reaction, the most notable being oxidation processes. In such cases the reagents glow although their temperature is far lower than that necessary to produce the glow by temperature radiation. Well-known examples of this "cold light" are the oxidation of phosphorus, the glow of various insects (glow-worms, fire-flies, &c.), and "phosphorescence" of the sea. Investigations, especially with gases (see below), have led to the view that the processes involved are more or less similar to those of fluorescence (particularly sensitized fluorescence (p. 161)) but that the energy transferences, instead of being from molecules excited by absorption of light, are from molecules possessing as extra potential energy the whole or part of the energy of reaction of a chemical process, i.e. molecules excited by the chemical reaction. Various cases are possible according as the substance capable of fluorescence is one of the orginal reacting substances, one of the products of reaction, or some foreign admixture which may take up the energy liberated.

The following are some cases of reactions giving very intense chemiluminescence.

(*a*) A mixture of 10 c.c. of 10 per cent pyrogallol solution, 10 c.c. of 40 per cent potassium carbonate solution, and 10 c.c. of 35 per cent formaldehyde solution is rapidly treated with 20–30 c.c. of 30 per cent H_2O_2 (all reagents being in aqueous solution). A very intense red glow is obtained.

(*b*) Another striking reaction is the oxidation of the unsaturated silicon compound, silical hydroxide $Si_2O_2H_2$, by means of permanganate. To demonstrate this, we take a large flask containing a rather thick paste of dilute hydrochloric acid and silicon partly decomposed and turned yellow after long treatment with boiling water. A number of potassium permanganate crystals are added in the dark and the whole swirled round vigorously. A very intense yellow glow is produced. Preparation of the silicon: roughly broken calcium silicide is placed in a glass flask, covered with fuming hydrochloric acid cooled in ice, and the mixture allowed to react for several hours, cooled all the time (if necessary with a freezing mixture). When effervescence ceases the contents of the flask are diluted with cold water and filtered off as rapidly as possible on the suction filter, using a water-jet aspirator. The residue is washed with aqueous alcohol. It is very remarkable (and important for the theory of chemiluminescence) that the silical hydroxide itself may be made to fluoresce very strongly by excitation with light. Another observation which furnishes evidence for the theory of energy transference is that silical hydroxide can be coloured with dyes and that in the oxidation it is then the fluorescence of these dyes that is emitted.

The glow of certain living creatures (*bioluminescence*) is due to the oxidation of a substance called *luciferin* in presence of an enzyme called *luciferose*. The oxidation is reversible: the oxidation product can be reduced so as to give luciferin again. The spectral distribution of the emitted light is extremely favourable for visual purposes (fig. 43). Thus nature has actually solved the problem of the most rational production of light. Since the processes giving rise to the emission of the light can take place outside the living organism, their technical development (e.g. on the basis of electrolytic oxidation and reduction) is by no means inconceivable. Radiation (in the ultra-violet) is also supposed to be emitted in the course of active cell division (the so-called *mitogenetic rays*). Rays of the same wave-length are supposed to exert a very marked influence on cell-division phenomena. The existence of these rays, however, is still contested.

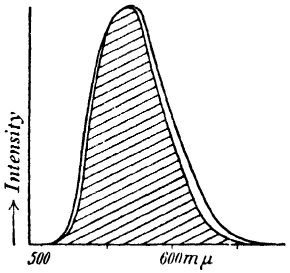

Fig. 43.—Spectral distribution of energy in the light emitted by fireflies. The shaded area shows the energy utilized by the eye. (Cf. Vol. IV, fig. 20, p. 31, which shows the efficiency of a good incandescent lamp.)

Quantitative experiments on the luminescence accompanying chemical reactions can best be carried out with gases. For example, when sodium vapour mixed with nitrogen is allowed to flow into an atmosphere of chlorine (Haber and Zisch), a glowing flame is obtained with a temperature of only 50–60° C. The observed strong emission of the D lines must be due to transference of excitation energy to sodium atoms on collision with newly formed NaCl molecules containing the whole or a part of the reaction energy stored up in them. A number of different reactions were found to occur in the sodium-chlorine flame, the one giving rise to the luminescence being $Na_2 + Cl = NaCl + Na + 75$ cal. Detailed investigation showed that the energy of reaction remains stored up in the NaCl molecule and is then transferred to a sodium atom by a collision of the second kind. The energy required to excite a D line is 48·3 cal. per gramme-atom (see p. 179). Another example that has been investigated in detail (by Bonhoeffer) is the transference of the energy of the reaction $2H = H_2$ to foreign metallic atoms present as vapour. Here we seem to be concerned with the simultaneous collision of two hydrogen atoms with a metal atom (triple collision), the taking up of the energy of reaction by the metal atom making possible the formation of an H_2 molecule. The energy absorbed by the metal atom (Na or Cd) may then be re-emitted as light.

Photo-chemical Reactions.—The reverse of chemiluminescence is the occurrence of chemical reaction as the result of illumination. Such phenomena are very widespread; we need only call to mind the bleaching action of sunlight and the assimilation of carbon dioxide under the influence of the sun's radiation (see below). Organic growth also seems to be intimately bound up with chemical processes which are produced by light (chiefly ultra-violet light).

The experimental data so far accumulated indicate that in most cases the first process is the absorption of light by an atom or molecule, which thereby passes into an excited state. The energy of excitation can then be passed on in collisions so as to give rise to chemical reaction. In certain cases (so-called **chain reactions**) the ensuing changes may be such that fresh reactive atoms or molecules are continually produced, so that the reaction (when once started) may go on without the further agency of light. An example of this is the combination (explosion) of chlorine and hydrogen under the action of light. In cases of this kind light can only have an accelerating (or possibly retarding) effect on the reaction. In other cases, however, while each excited molecule may undergo a certain reaction, no further molecules are thereby excited to react and hence no chain of reactions is set up. An example is the decomposition of HI under the action of light, which may be represented as follows: $HI + h\nu \rightarrow HI^*$; $HI^* + HI \rightarrow H_2 + I_2$. Here $h\nu$ is the absorbed light quantum and the asterisk denotes excitation. Thus two molecules of HI are decomposed for each light quantum absorbed. A remarkable result (and one which is of great importance for the theory of photo-chemical reactions) is observed when the region of absorption is wide, i.e. when light of considerably differing frequencies can be absorbed. Since each light quantum gives rise to one elementary reaction, and since the number of light quanta per unit of energy (say per erg) is greater for small values of ν (p. 125), the quantity of material reacting as the result of absorption of unit energy must be greater for light of low frequency (long wave-length) than for light of higher frequency (shorter wave-length). Actually it is observed that, for the same amount of energy absorbed, the quantity of HI decomposed is 1·45 times as much for light of wave-length 2820 Å. as for light of wave-length 2070 Å. (calculated ratio, 1·35).

It must be assumed that the excess of energy on absorption of a larger light quantum is transformed into thermal energy (p. 126). It may happen (especially in presence of an inert medium) that the excited atom or molecule may collide with an inert atom or molecule and so lose its energy of excitation before meeting with an atom or molecule with which it could react. In such a case the excitation energy is eventually transformed into heat. This accounts for the fact that the observed yield is often considerably smaller than that which would be expected on the basis of one elementary reaction for each absorbed light quantum.

A good example of a photo-chemical reaction is the dissociation of H_2 under the action of the line 2537 Å. in presence of mercury. A quartz tube filled with H_2 contains a little CuO and mercury. Irradiation with the mercury resonance line 2537 Å. (from a cooled mercury arc, with precautions to prevent self-reversal) causes reduction of the CuO to copper. This is manifested by the reddish colour produced. No reduction takes place on irradiation of H_2 in absence of mercury nor of mercury in absence of H_2.

The energy required to dissociate H_2 is $6{\cdot}9 \times 10^{-12}$ erg. The energy of the quantum of the resonance line 2537 Å. is $7{\cdot}7 \times 10^{-12}$ erg. Hence although the direct dissociation of H_2 by the action of the light is impossible because H_2 does not absorb in this region, the dissociation becomes possible by the transference to the H_2 molecule of the energy of excitation of an excited mercury atom. The processes occurring can thus be represented as follows: $Hg + h\nu \rightarrow Hg^*$; $Hg^* + H_2 \rightarrow Hg + 2H$. The atomic hydrogen then reduces CuO to copper with formation of H_2O. This experiment also throws light upon the great capacity of H_2 for quenching the resonance fluorescence of mercury (p. 160).

An example in which chain reaction gives rise to a much bigger yield than that anticipated from the amount of light absorbed, is the formation of ethane, C_2H_6, from ethylene, C_2H_4, and hydrogen, H_2, by the action of atomic hydrogen. The processes taking place are probably as follows: $C_2H_4 + H \rightarrow C_2H_5$; $C_2H_5 + H_2 \rightarrow C_2H_6 + H$. Then $H + C_2H_4 \rightarrow C_2H_5$, &c., until the collision of a hydrogen atom with another hydrogen atom stops the chain with formation of H_2. If the atomic hydrogen is formed by irradiation of H_2 in presence of mercury vapour (as described above), the number of C_2H_6 molecules formed per light quantum absorbed may be very large.

The Photographic Process.—One of the most important technical applications of photo-chemistry is in photography. The photographic process, i.e. the change brought about by light in silver halides (especially AgBr) embedded in gelatine or collodion, is characterized by the fact that in the first place no visible effect is produced in the photographic plate (formation of *latent image*). The silver halide grains which have been affected by light are brought into a certain state in which they can be reduced by a suitable " developer ". In development they are reduced to silver, and, if the process is suitably controlled and the original exposure to light not too long, the density of the silver deposited is greatest where the illumination was most intense and hence the absorption of energy greatest. Of course the process of development must be carried out in the dark (or at least in some light—usually red—to which the plate is not sensitive). After development the unaffected silver halide is dissolved out in a suitable " fixing bath " (usually " hypo ", $Na_2S_2O_3$), leaving the silver image behind.

As can be seen from their yellow colour, ordinary silver halide emulsions have an absorption spectrum lying in the short-wave visible region, so that blue and violet light are alone photographically effective. The emulsions will, however, adsorb dyes with absorption regions of longer wave-length, and it has been found that with suitably chosen dyes the energy absorbed is transferred to the silver salt and so goes to form a latent image (so-called *sensitization* (Vogel, 1873)). In this way it is now possible to make plates sensitive to all spectral regions up to about $1{\cdot}2\mu$ in the infra-red. On the other hand, the plates can be allowed to adsorb certain dyes after exposure, with the result that their sensitiveness is so far reduced that development can be carried out by candle-light (so-called *desensitization* (Lüppo-Cramer, 1921)). Ordinary photographic plates are also unsuitable for light of very short wave-length, on account of absorption in the gelatine. In such cases it is necessary either to use gelatine-free plates (Schumann plates) or else to smear the ordinary plates with some liquid (machine oil) which fluoresces when illuminated with light of short wave-length. As Pohl and his collaborators have shown, an elementary process corresponding to the formation of a latent image occurs in many crystals on absorption of light of suitable wave-length. For the alkali halides (e.g. KBr) the wave-length is usually very short, corresponding to the absorption distribution of these substances. The crystals thereby become coloured. Thus with sufficiently thick layers of KBr a blue tint is observed. The fact that the latent image in photographic plates is invisible is therefore due to the thinness of the layer. If sufficiently thick AgBr crystals are used, the latent image produced by illumination can easily be seen. The coloration is due to the appearance of a new absorption region of longer wave-length—a state characterized by loosely bound electrons (p. 129). The chemical development of the image is obviously a problem for colloid chemistry. In certain circumstances the initially atomic products of reaction can coagulate and so form nuclei for the deposition of the metallic silver liberated by the reducing agent used as developer.

The Assimilation of Carbon Dioxide.—The most important photo-chemical reaction in nature is the assimilation of atmospheric carbon dioxide (concentration 0·03 per cent) by green plants. Under the influence of sunlight plants are able to split off the oxygen and combine the carbon with water. The mechanism of these phenomena still remains somewhat obscure. The products of the reduction are carbohydrates, the raw materials for the building up of the illimitably varied organic compounds which play such an important part in the life of plants and hence also in the life of animals. The necessary energy for the life processes of practically the whole of the living world is derived from the reversal of this assimilation process, i.e. by the oxidation of carbohydrates to carbon dioxide and water. The fuel is thus provided by the substances synthesized by plants in the photo-chemical process of CO_2 assimilation, and the store of energy in the fuel is derived in the last resort from the sun's radiation.

The assimilation of CO_2 only takes place in presence of a green substance (the green of leaves, called chlorophyll). The simultaneous co-operation of an unknown colourless protein (a so-called enzyme) seems also to be indispensable.

13. Phosphorescence

Phosphors.—In what follows the term *phosphor* * will be used to denote a substance which, as the result of suitable excitation, is able to go on emitting light (not temperature radiation) after the excitation has ceased. A systematic investigation of phosphorescence became possible after Lenard and Klatt had elucidated the chemical structure of an important class of phosphors, the alkaline-earth sulphide phosphors (see below). Lenard also developed the fundamental concepts upon which quantitative studies must be based.

In most cases the persistent after-glow is not simply a property of the substance which forms the bulk of the phosphor (e.g. alkaline-earth sulphide or oxide, or organic substances—mostly colloidal—such as gelatine or frozen alcohol). It is to be regarded as due rather to *traces of heavy metals or organic substances* (generally aromatic) embedded in the main substance.

This does not mean that mere mixture of the main material with the heavy-metal or organic impurity will give a phosphor. A special kind of combination is necessary: the phosphor must be *prepared*. For all the purely inorganic phosphors which have hitherto been investigated in detail, this process of preparation consists of heating the ingredients together. In order to obtain a good after-glow it is usually necessary to use as flux a concentration of 1–10 per cent of a colourless salt with a relatively low melting-point, though direct melting is also possible. In certain cases it seems that the particular structure requisite for phosphorescence can be attained by treatment with energetic electromagnetic or electric rays. Extremely small quantities of impurities may give rise to after-glow effects. Thus as little as 0·000006 gm. of copper in 1 gm. of ZnS, or 0·0000001 gm. of fluorescein in 1 gm. of boric acid, may produce strong phosphorescence.

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* Gr. *phōs*, light, *phoros*, bearer.

The only pure substance which shows an after-glow of long duration is solid nitrogen (VEGARD).

Examples of Phosphors.—Very brightly phosphorescent preparations can be made as follows.

Alkaline earth sulphide phosphors (so-called LENARD phosphors). The raw material is the carbonate or oxide. This is heated to redness with sulphur (0·7 gm. S to 1 gm. CaO; 0·4 gm. S to 1 gm. $SrCO_3$; 0·22 gm. S to 1 gm. $BaCO_3$). The product—referred to below as "sulphide"—contains, in addition to the sulphide, considerable quantities of sulphate and other sulphur compounds.

CaS-Bi.—5 gm. of calcium "sulphide" + 0·25 gm. Na_2SO_4 + 0·15 gm. $Na_2B_4O_7$ + 0·1 gm. CaF_2 + 0·0012 gm. Bi are heated together to bright redness for 25 min. in a furnace. This preparation phosphoresces very brightly and very persistently with a blue colour.

BaS-Cu.—3 gm. of barium "sulphide" + 0·05 gm. Li_3PO_4 + 0·00024 gm. Cu are heated together to moderate redness for 15 min. This gives a very bright orange-red phosphorescence.

The commercially obtainable zinc sulphide phosphors (Sidot blende), which contain traces of copper as active impurity, also exhibit a very bright after-glow. Phosphorescent preparations can also be made by embedding certain organic substances in gelatine, sugar, frozen alcohol, &c. The boric acid phosphors give very intense effects (TIEDE). An example of a preparation is as follows: powdered boric acid is treated with terephthalic acid or the sodium derivative of fluorescein in the ratio of 1 : 1000 or 1 : 3000 respectively. The mixture is then heated to melting-point on a tinned iron sheet. When cold, excitation with the light of an iron arc (which is strong in ultra-violet) produces a beautiful after-glow of blue or yellow-green colour respectively.

Spectral Distribution of Emission and Excitation.—The light emitted by phosphors is usually spread out over a wide range of wave-lengths. The spectrum may contain either diffuse bands (as in fig. 42, p. 161), bands with a structure (fig. 40, p. 159), or sharp lines (fig. 41, p. 160). Any spectral region characterized by a common rate of emission and common temperature dependence is referred to as a phosphorescence *band*, no matter what its structure and position. The so-called *distribution of excitation* is obtained by plotting the wave-lengths of the exciting light as abscissæ and the corresponding intensities of after-glow as ordinates. This distribution consists in nearly all cases of diffuse bands, corresponding to the spectral distribution of the absorption of the phosphor (fig. 44); for only absorbed light can cause excitation. The absorption of the light produces changes in the phosphor. Thus a new region of absorption (of longer wave-length) makes its appearance when the phosphor becomes excited (see also p. 129), while the absorption in the region of the distribution of excitation becomes less.

The Storing Up of Energy in Phosphors.—Almost all phosphors, in addition to their after-glow, exhibit an emission of light *during* illumination (instantaneous effect). In what follows we shall ignore this phenomenon, which is related to fluorescence, and consider only the persistent effect.

Both the brightness and the duration of the after-glow are functions of the preparatory treatment and the temperature, the dependence upon these factors being very different for different " bands ".

All bands have the common property of disappearing above a certain temperature, the value of which varies from band to band. In the same way there is in general a certain minimum temperature below which the bands exhibit no glow, although excitation energy is stored up. Between these upper and lower temperature limits, the upper and lower *instantaneous states*, extends the region of persistent after-glow.

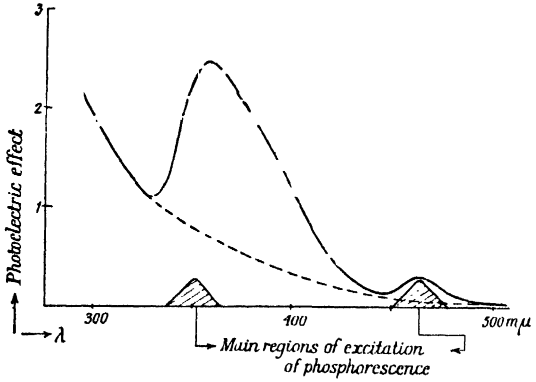

Fig. 44.—Spectral distribution of the external photoelectric effect of a CaS-Bi phosphor

In the lower instantaneous state storing up of energy occurs, but there is no after-glow. In the intermediate region simultaneous storing up and re-emission take place.

Great interest attaches to the effect of temperature variations after excitation. For simplicity we consider a phosphor with only one band. If this is exposed to exciting light at a temperature below the lower limit of after-glow, then when the illumination is cut off no glow is observed. But if the temperature of the phosphor is then raised, without any further excitation, emission of light starts spontaneously. Mere rise of temperature without previous excitation produces no such glow. The effect may be regarded as a driving out of the previously stored energy by the heat. This driving out may take place all at once or in any number of stages. Each successive heating up can cause the emission of light only to the extent left over from the previous heating. Hence this appearance of a glow as the result of rise of temperature must not be regarded as a special kind of excitation of the phosphor by addition of heat, but merely as an emission of previously stored energy made possible by suitable adjustment of the temperature conditions.

Displacements of Electricity in Phosphors.—It is found that the excitation of phosphors is always accompanied by a photoelectric effect at their surfaces. This is definitely associated with phosphorescent properties, and the non-phosphorescent constituents of the phosphors do not show the effect. The connexion with phosphorescence becomes even clearer in view of the fact that only those wave-lengths can produce the photoelectric effect which can also excite an after-glow (fig. 44). In the case of good CaS-Bi-phosphors the effect is almost as great as in freshly polished magnesium metal. The photoelectric effect appears only during the excitation of the phosphors; there is no appreciable liberation of electrons during the after-emission. Phosphors also show an internal photoelectric effect: displacements of electricity are associated with both excitation and after-emission, and these are completely analogous to the displacements investigated by Pohl and his collaborators in photoelectrically conducting crystals (p. 128). Phosphorescence represents a special case of this general behaviour, the special arrangement of the group of molecules making an emission of light possible as an accompaniment of the motion of electric charges, even in the solid state.

Light-sum.—Lenard gave the name *light-sum* * to the amount of light energy stored up in a given phosphor at a given instant. Use of this very important concept enables us to give a good quantitative description of the behaviour of phosphors. During excitation the light-sum stored up in the phosphor approaches a limiting value, the magnitude of which increases with the exciting intensity but can never exceed a certain maximum. For constant incident intensity the light-sum approaches a limiting value, the rate of approach being greatest when the incident intensity is greatest. The maximum possible light-sum for any intensity or duration of excitation is called the *complete light-sum*. Measurement of the complete light-sums of phosphors containing different amounts of metal at first shows an increase in proportion to the metal content; but after a certain value is reached (for CaS-Bi this value is reached for a concentration of only 0·00002 gm. Bi per gm. CaS) the light-sum increases no further as the metal content is increased. The complete light-sum for excitation with monochromatic light is a function of the wave-length, being greatest for wave-lengths near the maxima of the excitation distribution.

Rate of Decrease of Light-sum in After-emission.—Observation shows that the brightness of the after-glow dies out progressively from the moment when the excitation is cut off (fig. 45). Introducing Lenard's concept of light-sum, we may state the law of decrease (first discovered by Lenard) in the following way: in all cases the decrease can be simply represented as the sum of a number of exponential functions. The higher the temperature, the more rapid is the rate of decrease of the light-sum. Infra-red light of certain wave-lengths has the same effect as rise of temperature. Certain spectral regions in the infra-red, however, inhibit the after-glow.

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* Ger. *Lichtsumme.*

The last effect can be shown especially well with ZnS-Cu. A large area of this phosphor is excited by means of an incandescent lamp. It is then placed in the dark, and the image of the crater of an arc is focussed sharply upon the glowing surface with a suitable filter (e.g. iodine in CS_2) interposed to cut off all the visible light and let through only the invisible infra-red. A dark spot is at once observed on the phosphor at the spot where the infra-red rays fall upon it.

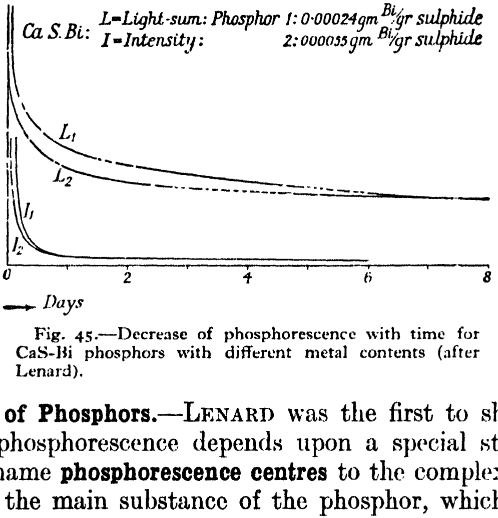

Fig. 45.—Decrease of phosphorescence with time for CaS-Bi phosphors with different metal contents (after Lenard).

Structure of Phosphors.—Lenard was the first to show that the property of phosphorescence depends upon a special structure, and he gave the name **phosphorescence centres** to the complexes of atoms, embedded in the main substance of the phosphor, which possess the property. The number of atoms in a complex is of the order of 10^3–10^5. It is clear that the self-contained fields of force necessary for appearance of an after-glow, and the energy insulation of the phosphors which makes possible a storing up of energy over measurable periods, can only occur in very complex aggregates.

In crystalline substances such as ZnS, zinc silicate, or the halides, the centres are probably small micro-crystalline regions with good thermal insulation from their surroundings. Thus a necessary condition is a discontinuity in the lattice of the crystal. Such discontinuities seem to be caused partly by the presence of atoms of the heavy metal (e.g. Mn or Cu in ZnS) which is foreign to the lattice, and partly by natural inhomogeneities in the crystal. In agreement with this it appears that the presence of such primary crystal irregularities is necessary for the production of phosphorescent properties in rock-salt by pigmentation with fast cathode rays. The investigations of GUDDEN and POHL upon photoelectric conductivity in well-defined NaCl crystals containing foreign atoms have thrown considerable light (p. 128) upon the questions of the liberation of electrons in the interior of such lattices (corresponding to the excitation of phosphorescence centres) and the return of these electrons (corresponding to the after-glow).

Views concerning the Mechanism of Phosphorescence.—As early as 1904 LENARD and KLATT expressed the view that the excitation of a phosphor consists in the liberation of electrons from the heavy-metal atoms, and that in the after-emission of light these electrons return to their original condition. An electron thus split off from its parent centre is supposed to be held by the surroundings, until finally, after a definite average time depending on the temperature and the nature of the phosphor, it is (as it were) shaken loose again by thermal agitation and returns to its initial state. Other things being equal, the time of return depends on the statistical distribution of the energy of the thermal collisions, so that each kind of phosphorescence centre (characterized by its number of atoms and the corresponding degree of energy insulation from the surroundings) must show an exponential decrease of light-sum, as is actually observed. LENARD'S views have been extended in the course of subsequent investigations to give the following general theory.

The absorption and emission processes must be regarded as occurring in different spatial regions. The phosphorescence centres are supposed to consist of more or less firm combinations of the actual phosphorescent substance with large molecular complexes, the latter being characterized by the fact that their electron orbits form self-contained units (e.g. lattice blocks, organic aggregates, &c.) in which a free migration of energy is possible. In phosphorescence the energy is primarily absorbed in the molecules of phosphorescent substance in a centre and stored up in them as energy of excitation. Then as a result of thermal motions an excited molecule may collide with the large molecular complex. In a certain fraction of these collisions the energy of excitation will be transferred to the complex, which will then emit it as light. The wave-lengths emitted will thus be characteristic of the complex. This theory, according to which energy emission is preceded by transferences due to collisions of the second kind, is successful in explaining the constancy of the emission spectrum even when several electrons are liberated per atom of phosphorescent substance during excitation. It also accounts for the large effective cross-section of the centres, as well as their surprising insulation with respect to energy.

Historical.—In 1909 LENARD quite definitely expressed the view, based upon his experiments upon phosphors, that the emission of light from atoms is associated with the return of an electron to its initial state after excitation. This idea has been of the greatest significance for the development of the theories of light emission, and formed one of the foundations of the later theory of BOHR. A further clue was obtained in 1913 by LENARD and HAUSSER, again from observations of phosphors, by measuring the maximum amount of energy which could be stored up in a phosphor whose metal content was accurately known. In this way they gave the first answer to the question of how much energy an atom can emit after a single process of excitation. They were able to show that the amount is of the same order of magnitude as the emitted light quantum. This indicates that the elementary process of light emission involves "packets" of energy (or light quanta)—a conclusion which has been borne out in an even more striking manner by subsequent experiments, especially those on the transference of energy by electron collision (p. 51).

E. The Emission of Light and the Model of the Atom

14. The Fundamental Laws of Absorption and Emission of Energy by Atoms

The following laws of the interaction of light and matter have already been met with:

1. When light of frequency ν is absorbed by matter, the quantity of energy $h\nu$ may be taken up by an electron, which as a result may be ejected from the atom (and in some cases from the macroscopic surface of the body). In this process the work of separation p is performed, so that the final kinetic energy of the liberated electron is given by

$$\tfrac{1}{2}mv^2 = h\nu - p.$$

2. When kinetic energy is taken up by an atom or molecule from an impinging electron or material particle, the collisions may be inelastic if the energy of the impinging particle exceeds a certain definite minimum. As soon as this minimum is exceeded, monochromatic light of frequency ν is observed to be emitted. The frequency satisfies the relation $h\nu = \frac{1}{2}mv^2$.
3. The phenomena of fluorescence show that atoms can be made to take up different discrete excited states, from which they may return to the normal state by emission of light. Provided that the emitting atoms are unperturbed, the light they send out is monochromatic.
4. The phenomena of phosphorescence show that the processes of excitation and return to normal during after-glow are associated with the motion of electrons.

In 1913 Niels Bohr summarized the above conclusions in the two following postulates, which form the basis of modern atomic theory:

1. *An unperturbed atom can exist in definite stationary states, each of which corresponds to a definite energy of the system. The transition from one stationary state to another is accompanied by emission or absorption of light, the energy given out or taken in being equal to the difference between the energies of the two stationary states in question.*
2. *The emission of radiation by an atom or molecule is due to the transition from a stationary state of energy* E_n *to a second stationary state of lower energy* E_m. *The frequency* ν *of the radiation follows from the*

fact that the energy of the corresponding quantum is equal to the difference between the energies of the two stationary states concerned, i.e.

$$h\nu = \frac{hc}{\lambda} = E_n - E_m.$$

In the same way the absorption of radiation by an atom or molecule is due to the transition from a stationary state of energy E_m *to a second stationary state of higher energy* E_n, *the difference* $E_n - E_m$ *being equal to the quantum* $h\nu$ *of the absorbed light. If the atom has no stationary state of energy* E_n *fulfilling this relationship, then there is no absorption: the light passes on and the atom is left in its original state after temporary perturbation by the incident electromagnetic field.*

These postulates may be represented graphically as follows. In fig. 46 let E_0 represent the energy of the system (atom or molecule) in the normal or ground state. Experiment (e.g. on the absorption by excited atoms, p. 157) shows that every atom returns to this ground state very soon after any alteration of its energy. The time-lag is usually of the order 10^{-8} sec., though in special circumstances it may be as high as 10^{-3} or 10^{-2} sec. in gases. Here it is assumed that no electron is completely separated from the atom; for it is known that an ionized atom may remain in the ionized state for an indefinite period of time, provided that the experimental conditions are suitably chosen. This stable ionized state may be regarded as the ground state of the ion, which can be further excited. According to ordinary macroscopic mechanics or electrodynamics, a system may take up energy in indefinitely small amounts. This is represented in fig. 46 by the continuous range of possible energies on the left. The experiments described above show that conditions are quite different for atoms; in general, in fact, an individual atom must be supplied with at least a certain minimum quantity of energy before it can absorb any at all as *internal* energy. On the other hand, however, the taking up of energy as *kinetic* energy relative to the surroundings can take place continuously in all cases realizable in practice (see also gas degeneration, Vol. II, p. 151). In the figure E_1 represents the next possible value of the internal energy above the ground state E_0. Above E_1 are the further possible states of higher energies E_2, &c. (cf. the experiment described on p. 51). Thus in place of the "classical" continuum we have a number of distinct and definite values for the energy. One of the **fundamental problems of atomic physics** is to investigate these discrete energy levels of atoms and molecules, as well as the possibilities of transition from one to another.

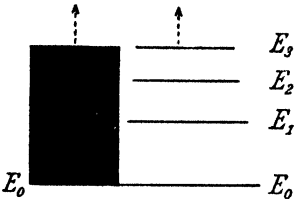

Fig. 46.—Permitted energy states of a classical system (left) and an atomic system (right).

Measurement of Energy.—Experiment can only give the differences between the energy of one state and the energies of other states. Hence the energy E_0 of the ground state may be taken as zero. This is the only convention which is generally adopted (see also p. 181).

As regards units, it is not usual to express the energies in ergs per molecule or per atom,* since in many cases it is more convenient to use other units. The following are in use:

(*a*) Cals./mol, i.e. the energy per gramme-molecule. Here we have 1 cal./mol = (1/N) cal./molecule = (J/N) ergs/molecule, where N is Avogadro's number (Vol. II, p. 52) and J is the mechanical equivalent of heat (Vol. II, p. 32).

(*b*) Volts, or, more accurately, electron-volts (*e*-volts); here 1 *e*-volt is the kinetic energy attained by an electron in falling through a potential difference of 1 volt. Since $e = 1{\cdot}59 \times 10^{-20}$ e.m.u., and 1 volt $= 10^8$ e.m.u., it follows that 1 electron volt $= 1{\cdot}59 \times 10^{-12}$ ergs.

(*c*) Frequency ν. This expresses the frequency (in sec.$^{-1}$) which a light quantum would have to possess in order that its energy should equal the energy in question, i.e. $\nu = E/h$.

(*d*) Wave-number $\bar{\nu}$. The *wave-number* is the number of wave-lengths of an electromagnetic radiation per centimetre of path in vacuum. The equation $\nu = c\bar{\nu}$ is obviously true, c being the velocity of light (3×10^{10} cm./sec.). This method of expression gives the wave-number which a light quantum of the energy in question would possess.

(*e*) Wave-length λ. This unit is related to the preceding; it is the wave-length of a light quantum of the energy in question. The relationships between these different ways of expressing energy values are given in Table XVI.

As an example we may take the energy difference ($7{\cdot}73 \times 10^{-12}$ erg) between the ground state E_0 of the mercury atom and the next higher state attainable by irradiation. This energy difference is equivalent to the energy of a light quantum of wave-length 2536·7 Å. $= 2{\cdot}5367 \times 10^{-5}$ cm. or of wave-number 39422 cm.$^{-1}$ or of frequency $1{\cdot}183 \times 10^{15}$ sec.$^{-1}$; or to the kinetic energy of an electron which has fallen through a potential drop of 4·86 volts. For the sake of brevity we speak of the energy as being 4·86 volts (better electron-volts). From Table XVI we see, for instance, that an electron that has fallen through a potential drop of 1 volt would, if all its kinetic energy were transformed into radiation, give a quantum of wave-length $1{\cdot}233\mu$ and wave-number 8110 cm.$^{-1}$.

Representation of Emission and Absorption.—Consider an atom with the energy states E_0, E_1, E_2 . . . (fig. 47). The *absorption* of a light quantum of frequency ν_1, given by $h\nu_1 = E_1 - E_0$, corresponds to the transition from the state E_0 to the state E_1. This transition is represented by an arrow pointing from E_0 to E_1 as in the figure. Similarly, the absorption of a light quantum $h\nu_2 = E_2 - E_0$ is represented by the arrow between E_0 and E_2. The *emission* of the corresponding quanta is shown by arrows pointing in the opposite direction (see figure).

As we can see from fig. 47, an atom in the state E_1 may pass over into the state E_2 by taking in the amount of energy $E_2 - E_1$. Conversely, the return from E_2 to the ground state may take place in successive steps. This means that the excited atom in the state E_1 is

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* In what follows the word "molecule" will be used for the sake of brevity to cover both molecule and atom.

TABLE XVI.—RELATIONS BETWEEN THE QUANTITIES USED TO EXPRESS ATOMIC OR MOLECULAR ENERGIES

	ergs/molecule	cals./mol	electron-volts	ν(sec.$^{-1}$)*	$\bar{\nu}$(cm.$^{-1}$)†	λ(cm.)‡	T(° abs.)‖
ergs/molecule	1	$1{\cdot}44_7 \times 10^{13}$	$6{\cdot}28_1 \times 10^{11}$	$1{\cdot}53_0 \times 10^{26}$	$5{\cdot}10_1 \times 10^{15}$	$\frac{1{\cdot}96_1 \times 10^{-16}}{n}$	$4{\cdot}84_9 \times 10^{15}$
cals./mol	$6{\cdot}91_3 \times 10^{-14}$	1	$4{\cdot}34_8 \times 10^{-2}$	$1{\cdot}05_8 \times 10^{13}$	$3{\cdot}52_6 \times 10^{2}$	$\frac{2{\cdot}83_6 \times 10^{-3}}{n}$	$3{\cdot}35_2 \times 10^{2}$
electron-volts	$1{\cdot}59 \times 10^{-12}$	$23{\cdot}0$	1	$2{\cdot}43_3 \times 10^{14}$	$8{\cdot}11 \times 10^{3}$	$\frac{1{\cdot}23_3 \times 10^{-4}}{n}$	$7{\cdot}71_0 \times 10^{3}$
ν(sec.$^{-1}$)	$6{\cdot}53_5 \times 10^{-27}$	$9{\cdot}45_3 \times 10^{-14}$	$4{\cdot}11_0 \times 10^{-15}$	1	$3{\cdot}33_3 \times 10^{-11}$	$\frac{3 \times 10^{10}}{n}$	$3{\cdot}16_9 \times 10^{-11}$
$\bar{\nu}$(cm.$^{-1}$)	$1{\cdot}96_1 \times 10^{-16}$	$2{\cdot}83_6 \times 10^{-3}$	$1{\cdot}23_3 \times 10^{-4}$	$3{\cdot}00 \times 10^{10}$	1	$\frac{1}{n}$	$0{\cdot}950_4$
λ(cm.)	$\frac{1{\cdot}96_1 \times 10^{-16}}{n}$	$\frac{2{\cdot}83_6 \times 10^{-3}}{n}$	$\frac{1{\cdot}23_3 \times 10^{-4}}{n}$	$\frac{3{\cdot}00 \times 10^{10}}{n}$	$\frac{1}{n}$	1	$\frac{0{\cdot}950_4}{n}$
T(° abs.)	$2{\cdot}06_3 \times 10^{-16}$	$2{\cdot}98_5 \times 10^{-3}$	$1{\cdot}29_6 \times 10^{-4}$	$3{\cdot}15_6 \times 10^{10}$	$1{\cdot}05_2$	$\frac{0{\cdot}950_4}{n}$	1

* $h\nu$ ergs. † $hc\bar{\nu}$ ergs.

‡ hc/λ ergs. The λ values, which are the wave-lengths of the equivalent light quanta, must not be used directly as proportionality-factors. To obtain the λ-value corresponding to an energy which is n times that appearing in the same horizontal row, it is necessary to *divide* by n. This is indicated in the table.

‖ $3k\mathrm{T}/2$ ergs.

able to absorb light quanta of frequency $\nu_2 - \nu_1$. That this is in agreement with observation has already been pointed out on p. 157, and the excitation of mercury vapour by successive steps takes place in this way. Conversely, an atom in the state E_2 may either return to E_0 direct, thereby emitting the frequency ν_2, or may return to E_0 in successive steps, emitting the frequencies $\nu_2 - \nu_1$ and ν_1. Detailed investigation of the frequencies emitted in the experiments described on p. 157 shows that this conclusion fits the facts.

Selection Rules.—A restriction, which is of fundamental importance for the optical behaviour of atoms, has to be imposed on the above statements. It is found that certain transitions between the energy levels of an atom cannot be realized by absorption or emission of electromagnetic radiation. Suppose, for example, that an atom has the possible states E_0, E_1, E_2 . . . . Then it may well happen that, although the state E_2 can be reached from the ground state E_0 by absorption of a quantum of light of frequency ν_2, the state E_1 cannot be reached from the state E_0 by absorption. The atom is incapable of absorbing a quantum of the right magnitude, namely $h\nu_1 = E_1 - E_0$. This kind of incapacity is a fundamental property of atoms, and great importance attaches to the so-called selection rules that state which transitions between levels can actually occur by emission or absorption of radiation (or, as it is sometimes put, which levels can combine with one another).

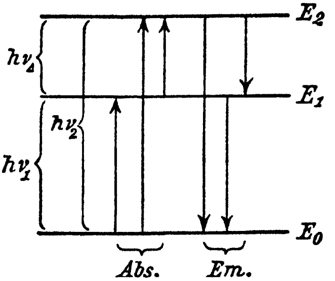

Fig. 47.—Diagrammatic representation of absorption and emission

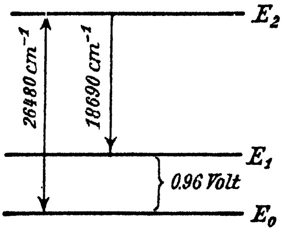

Fig. 48.—Longest-wave absorption of thallium and the corresponding emission.

One case of this kind we have already met with experimentally on p. 157. In resonance fluorescence various metal vapours give several lines in emission, although they only absorb one line. The explanation is as follows. (Fig. 48 is drawn to scale for thallium.) If we start from the state E_0, only the state E_2 can be reached by absorption. The state E_1 cannot be reached from E_0, although the transition between E_2 and E_1 and vice versa is quite possible. Hence the vapour absorbs as line of *longest wave-length* the line of frequency $\nu_2 = (E_2 - E_0)/h$; but two lines of frequencies ν_2 and $\nu_2 - \nu_1$ appear in emission. If, however, the vapour is heated above 800° C., the line of longest wave-length now absorbed has the frequency $\nu_2 - \nu_1$. From this we must conclude that at the higher temperature a sufficient number of the atoms possess so high an energy that their collisions result in excitation to the state E_1. These atoms, excited by collision, are capable of being further excited to the state E_2 by absorption of light of frequency $\nu_2 - \nu_1$. Measurements of the variation with temperature of the intensity of the absorption line of frequency $\nu_2 - \nu_1$ prove that this explanation is correct. From these facts we are led to the following very important conclusion, which is confirmed by many further investigations:

The selection rules hold only for transitions involving absorption or emission of radiation, not for transitions due to collisions.

In what follows we shall meet with a great many examples of this kind of reasoning and inference.

Spectral Terms.—According to what we have said above, the energy differences between the stationary states of an atom can be calculated from the lines of its spectrum. The frequency of any line can be written as the difference between two quantities known as *spectral terms*, namely

$$\nu = \frac{E_n}{h} - \frac{E_m}{h}.$$

As we have already mentioned on p. 157, the choice of the zero from which the energies are reckoned is arbitrary, since energy differences only are observable. While for most purposes it is simplest to take the ground state of the atom as zero, it is customary for historical reasons (on account of the simpler mathematical form assumed by certain relationships (see below)) to fix the zero at a level which exceeds this by the ionization energy. (For an exact definition see p. 191). As a result all the states of the neutral atom have *negative* energy values.

On account of the greater convenience of the numerical values involved, it is also customary to describe a radiation by its wave-number $\tilde{\nu}$ in cm.$^{-1}$, instead of by its frequency ν in sec.$^{-1}$. The two are related by the equation $\tilde{\nu} = \nu/c$. Thus the wave-number of a spectral line can be expressed as the difference of two *terms*, namely $\tilde{\nu} = T_m - T_n$, where $T_n = -E_n/(hc)$ and $T_m = -E_m/(hc)$. The terms so introduced are purely mathematical in character and are related to the energies of the atomic states in the way stated.

15. The Stationary Energy States of the Hydrogen Atom

We shall now turn to our main problem, which is the determination of the stationary states of atoms and their representation both mathematically and by means of models. Various sources of information have already been discussed above. Besides these, the spectral lines given by atoms during absorption or emission furnish a great deal of important evidence, partly because of the large number of the lines and partly on account of the accuracy with which they can be measured.

Spectral Series and Spectral Terms.—We will first show for the simplest example, hydrogen, how the energy states of the atom can be deduced from its spectral lines.

If hydrogen is excited to glow, e.g. in a Geissler tube, four lines are obtained in the visible region. They are given, with their usual names, in Table XVII (see also Vol. IV, coloured plate facing p. 158, No. 5).

TABLE XVII.—THE VISIBLE HYDROGEN LINES

H_α	$\lambda =$ 6562·99 Å.	$\bar{\nu} =$ 15232·97 cm.$^{-1}$
H_β	4861·52	20564·57
H_γ	4340·67	23032·31
H_δ	4101·94	24372·8.

Up to 20 lines can also be observed in the ultra-violet.

When the lines are plotted in a diagram (fig. 49), it becomes clear that the distances between successive members decrease regularly as we pass towards shorter wave-lengths. Such an array of lines is called a *series*. The members of the series become closer and closer together at the short-wave end, converging to a well-defined position called the *limit of the series*. The limit of the hydrogen series of fig. 49 lies at 3645·98 Å. In 1885 BALMER * succeeded in deducing the law of this series from the four visible lines. The series is called the BALMER series in his honour. His formula, in modern notation, is

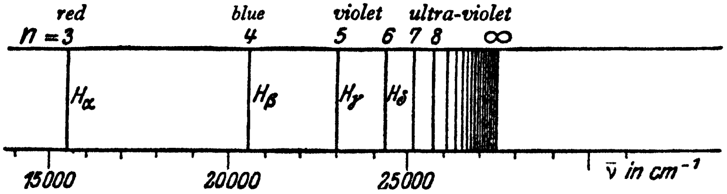

Fig. 49.—The Balmer series of hydrogen

$$\bar{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

where $R_H =$ 109677·76 cm.$^{-1}$ is a constant (now called the RYDBERG constant) and n is an integer which assumes the values 3, 4, 5 . . . for the successive lines of the series, beginning with H_α. In stellar spectra, as well as in that of the sun's chromosphere, up to 35 members of the

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*** JOHANN JAKOB BALMER (1825–1898) was a teacher in a girls' high school at Basle and lectured on descriptive geometry.**

series have been found in absorption. The limit of the series is obtained by putting $n = \infty$, which gives $\tilde{\nu}_{\text{limit}} = R_H/2^2$.

Further experimental investigation has revealed still more hydrogen lines which can likewise be arranged in series. Thus PASCHEN (1908) found some strong lines in the infra-red, the number of which was added to by BRACKETT (1922). The last worker also discovered another series in the long-wave infra-red. In 1924 PFUND observed a line of even longer wave-length. A new series was also found in the extreme ultra-violet by LYMAN (1916).

All these lines can be arranged in series with formulæ analogous to the BALMER formula, the only difference being that the number in the denominator of the first fraction varies from case to case, as follows:

$$\text{LYMAN Series: } \tilde{\nu} = R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \qquad n = 2, 3, 4 \ldots$$

$$\text{BALMER Series: } \tilde{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, 5 \ldots$$

$$\text{PASCHEN Series: } \tilde{\nu} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \qquad n = 4, 5, 6 \ldots$$

$$\text{BRACKETT Series: } \tilde{\nu} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \qquad n = 5, 6, 7 \ldots$$

$$\text{PFUND Series: } \tilde{\nu} = R_H\left(\frac{1}{5^2} - \frac{1}{n^2}\right), \qquad n = 6, 7, 8 \ldots$$

Here it should be particularly noted that the constant R_H is the *same* for all the series, so that all the lines of the hydrogen spectrum can be expressed by means of one general formula

$$\tilde{\nu} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

in which m and n are integers.

One of the essential features of this formula is that each spectral line is represented as the difference between two expressions of the form R_H/a^2, one of which is constant throughout a series, while the other assumes successive different values. Thus there is a parallelism to BOHR's formulation, according to which the frequencies of the spectral lines are proportional to the differences of the energies of two atomic states.

Combination Principle.—The regularities just described also throw light on a relationship, known as the *combination principle*, which had been discovered by RITZ long previously. RITZ noticed that addition or subtraction of the wave-numbers of two or more spectral lines usually gives the value for another line of the same atom. According to the above discussion, the explanation lies in the fact that each line may be regarded as given by the difference of the energies (or the terms) of two states. Thus if we have two lines corresponding to the term-differences $T_3 - T_1$ and $T_2 - T_1$, the difference of the two wave-numbers, $T_3 - T_2$, is again a possible spectral line, since T_3 and T_2 are terms belonging to two energy states of the atom. This fact has already been expressed graphically in fig. 47, p. 180.

Calculation of Terms.—The case of hydrogen may also serve to show how spectral terms are calculated from observed lines. We consider the following lines as known (wave-numbers in cm.$^{-1}$):

$\bar{\nu}_1 = 82258{\cdot}27$
$\bar{\nu}_2 = 97491{\cdot}28$
$\bar{\nu}_3 = 102822{\cdot}84$
$\bar{\nu}_4 = 105290{\cdot}58$
$\bar{\nu}_5 = 15232{\cdot}97$
$\bar{\nu}_6 = 20564{\cdot}57$
$\bar{\nu}_7 = 23032{\cdot}31$
$\bar{\nu}_8 = 5331{\cdot}52$
$\bar{\nu}_9 = 7799{\cdot}30$
$\bar{\nu}_{10} = 2469.$

Then we have $\bar{\nu}_5 = \bar{\nu}_2 - \bar{\nu}_1$; $\bar{\nu}_6 = \bar{\nu}_3 - \bar{\nu}_1$; $\bar{\nu}_7 = \bar{\nu}_4 - \bar{\nu}_1$; $\bar{\nu}_8 = \bar{\nu}_3 - \bar{\nu}_2 = \bar{\nu}_6 - \bar{\nu}_5$; $\bar{\nu}_9 = \bar{\nu}_4 - \bar{\nu}_2 = \bar{\nu}_7 - \bar{\nu}_5$; $\bar{\nu}_{10} = \bar{\nu}_4 - \bar{\nu}_3 = \bar{\nu}_7 - \bar{\nu}_6 = \bar{\nu}_9 - \bar{\nu}_8$.

All these lines can be regarded as combinations of five terms, namely

$T_1 = 109677{\cdot}7$
$T_2 = 27419{\cdot}4$
$T_3 = 12186{\cdot}4$
$T_4 = 6854{\cdot}8$
$T_5 = 4387{\cdot}1.$

Since we are concerned only with differences, all of these terms are of course indeterminate to the extent of an additive constant.

In the present case, however, the term values can be worked out directly from the series formulæ. Putting $n = \infty$ in each case, we obtain the values tabulated above, so that in this way the choice of the constant is decided. Further terms may also be calculated by analogy, i.e. by substituting higher integers for m in the constant R_H/m^2 of the series formulæ. In this way an array of terms is obtained like that illustrated in fig. 50, the wave-number scale of which is shown on the left-hand margin. This diagram is at the same time a representation of the energy states of the atom, the lowest levels (terms) representing the states of lowest energy. If the energy of the lowest state (the ground state) is arbitrarily taken as zero, then by means of the equation $E_n = -hcT_n + const.$ the energy values given in the right-hand margin may be worked out. Thus the energy-differences between the states of the hydrogen atom can be read off directly from the figure.

Only in the case of hydrogen can the whole spectrum be related to a single term-system like that given in fig. 50. For all other atoms the numerous and very complicated series relationships lead to several different term-systems. This complication will be discussed fully later (see Chap. V, p. 276).

Experiment shows that the zero-point chosen above for reckoning term-values, i.e. the level of highest energy, corresponds to the state whose energy is equal to the energy of ionization. Hence this is the state in which the atom has absorbed so much energy that the electron is completely removed from it.

The term-zero lies 109677·7 cm.$^{-1}$ above the ground state. Since 1 cm.$^{-1}$ = 1·23 × 10^{-4} electron-volt (Table XVI, p. 179), the corresponding energy difference is 13·53 electron-volts. Now from observations of resonance potentials (p. 51) it is possible to determine the stationary states of the atom empirically. Table XVIII contains the values determined by Compton and Olmstead (cf. fig. 50).

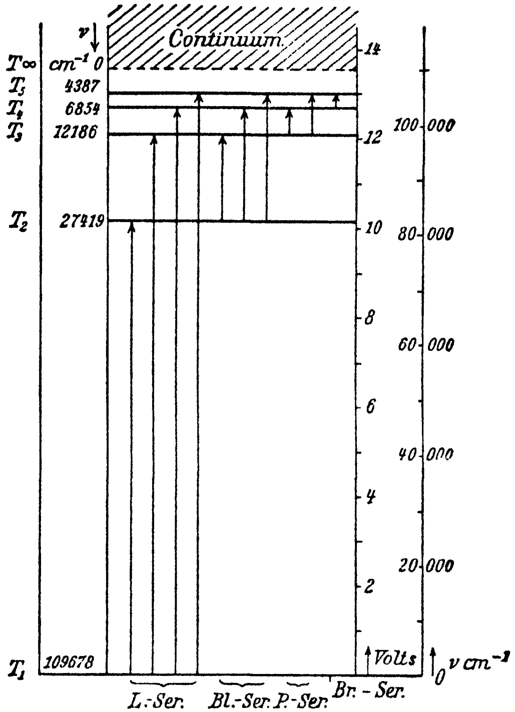

Fig. 50.—Term and energy level scheme for the hydrogen atom. The arrows indicate absorption

Table XVIII.—Determination of the Energy Levels of the Hydrogen Atom from Resonance Potentials

n	Volts (observed)	Volts (calculated)	n	Volts (observed)	Volts (calculated)
2	10·15	10·15	6	13·2	13·16
3	$12{\cdot}0_5$	12·03	7	13·3	13·26
4	12·7	12·69	—	—	—
5	13·0	13·00	∞	13·5	13·53

The table also contains for comparison the values calculated from the generalized Balmer formula. We see that the theory is actually in good agreement with the facts.

Inspection of fig. 50 shows that *the members of a series of emission lines are due to transitions from atomic states of different energies to a common end-state.* Since emission series can also be observed in absorption, it follows also that *a series of absorption lines is due to transitions from one and the same lower energy-level to different higher levels.* As was explained above, the limit of an absorption series corresponds to the process of ionization of the atom. Since this limit is taken as the zero from which term-values are reckoned, a knowledge of it enables us to calculate the value of the lowest term involved in the series. In this way the term-value of the ground state is obtained, and if we take the energy of this state as the zero of reference, the relative energies of other states may be calculated from the term-differences, which are the only quantities accessible spectroscopically.

16. The Rutherford-Bohr Model of the Atom

As has already been explained on p. 36, LENARD discovered that a large part of the effective volume of an atom is " empty ", i.e. that the material constituents of the atoms are concentrated within a very small space, which can be calculated from his experiments. On LENARD'S view, each atom consists of " dynamids ", i.e. pairs of elementary positive and negative charges. The view now accepted is due to RUTHERFORD (p. 82), who proved by experiment that all the positive constituents of the atom are closely concentrated in a region with a radius of about 10^{-12} cm. (the *nucleus*). Thus the whole atom with its radius of about 10^{-8} cm. consists of a nucleus, in which the positive charge and nearly all the mass are situated, and a number of surrounding electrons.

If elementary positive and negative charges are regarded as point-charges, it is impossible on purely classical principles (i.e. by applying the FARADAY-MAXWELL theory of macroscopic electric fields) to construct an atomic model possessing the properties just outlined. It is clear that the attractive force between the oppositely-charged constituents must be balanced by a force tending to keep them apart. In the case of heavy particles the only compensating force of this kind is a centrifugal force, analogous to that which makes the orbits of the planets in the solar system stable.

In the electrical case of the atom, however, such a model is not stable. An electric charge rotating in an orbit (i.e. moving with an acceleration, Vol. I, p. 52) must, according to classical theory, radiate electromagnetic energy into space in the form of waves. This loss of energy would have to be derived from the internal energy of the atom. This means that the electron, like a planet moving through a viscous medium, would fall into the nucleus. The fact that atoms can exist for extended periods without radiation of electromagnetic waves proves that, if we hold to the experimentally well-founded view that the elementary charges are points, it is impossible to construct a satisfactory atomic model on classical principles.

Bohr * put forward an atomic model harmonizing with the observed properties discussed above. He retained the idea of negative point-charges circulating in orbits about a positive nucleus; but, building upon the experimental facts, he introduced the new hypothesis that certain dynamical arrangements of the charges (in particular certain orbits of the electrons) are stable in the sense that they can continue to exist over extended periods without radiation of electromagnetic energy (so-called *stationary states*). This hypothesis was, of course, in direct contradiction to classical ideas. The stationary states derived from the model must naturally agree, as far as their energy differences are concerned, with spectroscopic observation. In particular, the relationship between emitted frequency and energy loss must be fulfilled.

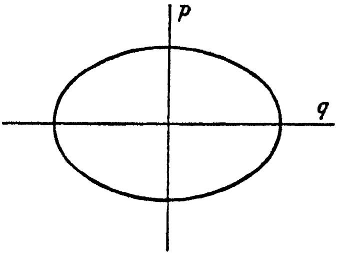

Fig. 51 -Phase diagram for the harmonic oscillator

The quantitative realization of Bohr's theory was made possible by applying the discovery (made by Planck in connexion with heat radiation, p. 150) that an atomic harmonic oscillator of frequency ν can only absorb or emit energy in integral multiples of a quantum of magnitude $h\nu$. When applied to the planetary model of nucleus and electron (so-called *rotator*), this quantum condition becomes as follows. *The angular momentum of the electron about the nucleus can only assume values which are integral multiples of an elementary value.*

This is often expressed by saying that the angular momentum is *quantized*.

Quantum Conditions for the Oscillator and the Rotator.—A short account will now be given of the basis of the calculation of the stationary states for the harmonic oscillator and for the rotator. We begin by considering a linear harmonic **oscillator,** a particle of mass m which can be displaced to either side of a mean position and which is acted upon by a restoring force proportional to the displacement. Its proper frequency ν is then independent of the amplitude a.

The displacement of the particle as a function of the time t is given by $q = a \sin 2\pi\nu t$. We also wish to consider the momentum p, which is given by $p = mv = m . dq/dt = 2\pi\nu ma \cos 2\pi\nu t$. In fig. 51 this momentum is plotted as a function of the displacement of the point, i.e. p is plotted against q, with rectangular axes. At its maximum displacement the particle is momentarily at rest, so that its momentum is zero. The maximum velocity, and hence the maximum value of the momentum, are attained on passing through the mean position ($q = 0$). Since the momentum involves the first power of the velocity, the sign of the momentum changes with the sense of the motion. Thus in the pq-plane (the so-called *phase-plane*) we get a closed curve like that shown in fig. 51. Elimination of t from the above equation readily shows that this curve (the so-called *phase diagram*) is an ellipse, since the equation between q and p is

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* Niels Bohr, born 1885; Nobel Prize winner; professor of theoretical physics at Copenhagen.

$$\frac{q^2}{a^2}+\frac{p^2}{b^2}=1,$$

where $b = 2\pi\nu ma$.

Now according to Planck the experimental investigations on heat radiation prove that only those states of an oscillator are possible whose energy differences relative to the ground state are integral multiples of an elementary quantity of energy $h\nu$. Applied to our phase diagram, this means that only a certain family of discrete ellipses is possible, and this family must be such that the differences between the energies corresponding to the different ellipses are integral multiples of $h\nu$. The energy of an oscillator is the sum of its kinetic energy $E_{\text{kin.}}$ and its potential energy $E_{\text{pot.}}$. As the particle passes through its mean position, $E_{\text{pot.}}$ becomes zero and $E_{\text{kin.}} = \frac{1}{2}m.a^2(2\pi\nu)^2 = ab\pi\nu$. But $ab\pi$ is the area of the ellipse, which must therefore be equal to W/ν, where W is the energy of the oscillator. We see that the area of the ellipse is proportional to the energy, and that, therefore, according to Planck's theory the only ellipses possible are such that the areas of successive members of the family differ by the constant area h (see fig. 52). The permitted ellipses are all similar, since $b/a = 2\pi\nu m =$ constant.

Hence if ΔW is the difference of energy between two successive permitted states of the oscillator, then $h = \Delta W/\nu$ and $\Delta W = h\nu$. The energy of the nth state is given by $W_n = W_0 + nh\nu$, the successive states being denoted by 0, 1, 2, 3 . . . from the ground state upwards. Thus the oscillator can only exist in certain definite stationary states, each of which is characterized by a certain ellipse in the phase-plane. Any alteration of the energy of the oscillator by absorption or emission must involve transition from one permitted phase ellipse to another.

The constant W_0 in the formula remains indeterminate. It is found, however, that if the oscillator is to persist as such its energy must not fall below a certain lowest level. As will be explained more fully later, this so-called *zero-point energy* comes out as equal to $\frac{1}{2}h\nu$.

The energy of the nth permitted state of a linear harmonic oscillator can therefore be written in the general form

$$W_n = (n + \tfrac{1}{2})h\nu.$$

In general (i.e. for a different mechanical system) the phase diagram will be of a different form. If we apply the formula $J = \int y\,dx$ for the area included between a curve $y = f(x)$ and the x-axis, the area of the closed phase diagram will be given in every case by the so-called *phase integral*

$$J = \oint p\,dq,$$

in which the circle through the integral sign indicates that the integration is to be taken once right round the closed curve.

If we generalize the quantum condition deduced above for the oscillator, the corresponding condition for any system can be formu lated as follows: *The difference between the phase integral of any two successive permitted states must be equal to h,* i.e.

$$\Delta J = h \quad \text{or} \quad J_n = J_0 + nh.$$

This condition holds in the general case for each degree of freedom of the system (Vol. II, p. 41). From the continuous range of mechanically possible motions it selects a discrete number of " quantized " motions as the only ones corresponding to stationary or permitted states of the system which are attainable by spontaneous adjustment.

The fact that these discontinuities cannot be detected in the case of ordinary mechanical systems is due to the extreme minuteness of the quantities of energy involved. The energy quantum for visible light ($\lambda = 5000$ Å.) is $h\nu = 3{\cdot}92 \times 10^{-12}$ erg. Even for the shortest γ-rays ($\lambda = 10^{-12}$ cm. approx.) $h\nu$ is only 2×10^{-4} erg. These, then, are respectively the mean and the maximum amounts of energy involved in atomic processes. They are extremely small relative to the energies involved in macro-mechanical processes, so that these processes show no sign of quantization. The difference is of the same kind as that met with in connexion with the structure of matter, where the macroscopic point of view gives the impression of a continuous character, though the underlying atomic or molecular structure is discontinuous.

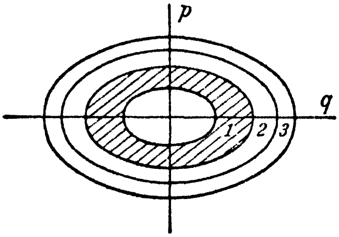

Fig. 52.—Representation of the permitted energy states of an atomic oscillator in the phase plane.

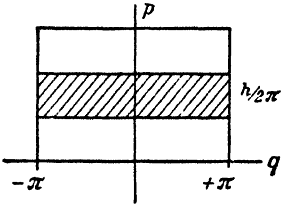

Fig. 53.—Phase diagram for the rotator

Owing to its importance in connexion with the atomic model, we must also consider the quantization of the **rotator**, i.e. a system in which a particle of mass m moves uniformly on a circle of radius a about a fixed centre. As q, the co-ordinate of position, depending on the time t, we take the angle φ described at the centre by the radius to the point. At time $t = 0$ we make $\varphi = 0$. Then we have $E_{\text{kin.}} = \frac{1}{2}ma^2(dq/dt)^2$ and $E_{\text{pot.}} = $ const., the radius a being constant for each stationary state. The corresponding momentum p, given as for the oscillator (p. 187) by the general formula

$$p = \frac{\partial E_{\text{kin.}}}{\partial\left(\frac{dq}{dt}\right)},$$

is here $p = ma^2(dq/dt)$, i.e. the angular momentum or moment of momentum of the point about the centre (see Vol. I, p. 136). This is constant for each stationary state. The phase diagram in the pq-plane is therefore a straight line parallel to the q-axis (fig. 53). One end of this line joins on to the other end after each revolution, however, since the phase of the rotator is repeated with the period 2π. The course of the motion in the phase-plane can best be pictured by imagining this plane rolled into a cylinder of circumference 2π. Then as the particle makes one revolution in its actual circular orbit, the corresponding point on the phase diagram passes once round the circumference of the cylinder, thereby arriving at its starting-point again.

The various permitted states of the rotator have different p-values, i.e. are represented on the phase-plane by parallel straight lines of length 2π at different heights above the q-axis. The area lying beneath the nth phase-line is $2\pi p_n$. According to the quantum condition, the corresponding area for the next permitted state must be given by $2\pi p_{n+1} = 2\pi p_n + h$. Putting $p_0 = 0$ for the lowest state (the justification for this will be apparent later), we obtain

$$2\pi p_n = nh.$$

Thus for a particle moving in a circular orbit the angular momentum must be an integral multiple of $h/(2\pi) = 1{\cdot}04 \times 10^{-27}$ erg-sec. The kinetic energy of the rotator is

$$E_{\text{kin.}} = \tfrac{1}{2}p\frac{dq}{dt} = \tfrac{1}{2}nh\frac{1}{2\pi}\frac{dq}{dt}.$$

Hence, since $\nu = \dfrac{1}{2\pi}\dfrac{dq}{dt}$,

$$E_{\text{kin.}} = n\frac{h\nu}{2},$$

where ν is the frequency of rotation of the rotator.

The energy of the rotator is seen to be quantized in half-energy elements or half quanta, each of magnitude $\tfrac{1}{2}h\nu$.

The Bohr Model of the Hydrogen Atom.—In its simplest form the model is as follows. An electron of charge $-e$ and mass m moves with constant linear velocity v or constant angular velocity ω in a circular orbit of radius a about a nucleus of charge $+Ze$ and mass M. The attractive force between the electron and the nucleus is given by the inverse square law. The nuclear mass M is assumed to be so large that the mass m of the electron is relatively negligible, and no account is taken of the change of the mass of the electron with change of velocity.

For each stationary state there is equilibrium between the electrical force of attraction and the centrifugal force acting upon the electron. Hence by Vol. I, p. 79, and Vol. III, p. 16 we have

$$\frac{mv^2}{a} = mv\omega = ma\omega^2 = \frac{Ze^2}{a^2}. \quad . \quad . \quad . \quad . \quad . \quad (\text{i})$$

Now for a rotator the angular momentum p must be an integral multiple of $h/(2\pi)$. Hence

$$p = mva = ma^2\omega = \frac{nh}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad (\text{ii})$$

where n is an integer. Division of (i) by (ii) gives

$$v = a\omega = \frac{2\pi Ze^2}{nh},$$

which on substitution in (ii) yields the result

$$a = \frac{n^2h^2}{4\pi^2mZe^2}; \quad \omega = \frac{8\pi^3mZ^2e^4}{n^3h^3}.$$

The period of revolution is given by

$$\tau = \frac{2\pi}{\omega} = \frac{n^3h^3}{4\pi^2mZ^2e^4}.$$

The important result is that the orbital radius a can only assume certain definite values and that these are proportional to the squares of the natural numbers. The number n is called the *quantum number* of the orbit.

Since for hydrogen we have $Z = 1$, the radius of the first permitted circular orbit becomes $a_1 = h^2/(4\pi^2me^2)$. The corresponding velocity of the electron is $v_1 = 2\pi e^2/h$ or, expressed as a fraction of the velocity of light, $\alpha_1 = \frac{v_1}{c} = 2\pi e^2/(hc)$. Substituting the numerical values, we get

$$a_1 = 0{\cdot}528 \times 10^{-8} \text{ cm.}; \quad \alpha_1 = 0{\cdot}00728.$$

The atomic diameter thus obtained (about 10^{-8} cm.) is in good agreement with experimental results on the size of atoms (Vol. II, p. 53) derived from quite different considerations.

The total energy W of the atom is given by $W = E_{\text{kin.}} + E_{\text{pot.}}$. Now we have

$$E_{\text{kin.}} = \tfrac{1}{2}mv^2 = \frac{2\pi^2mZ^2e^4}{n^2h^2}$$

and

$$E_{\text{pot.}} = -\frac{Ze^2}{a} = -\frac{4\pi^2mZ^2e^4}{n^2h^2} = -2E_{\text{kin.}}.$$

Hence

$$W = -\frac{2\pi^2mZ^2e^4}{h^2}\cdot\frac{1}{n^2}.$$

We see that the energy values of the system in the different states are inversely proportional to the squares of the respective quantum numbers and are negative in sign.

According to this the energy becomes zero for $n = \infty$, i.e. for an orbit with infinite radius, which means that the electron is completely removed from the nucleus or, in other words, the atom is ionized. For all orbits of finite radius the energy, reckoned relative to this zero, must be negative in sign, i.e. must be lower than for the orbit of infinite radius. The energy is lowest for the first quantized orbit ($n = 1$) and becomes higher as the quantum number increases. Thus we arrive in a rational way at the mode of reckoning energy already mentioned on p. 181.

Energy must therefore be supplied to the atom in order to cause the transition of an electron to an orbit of higher quantum number. On the contrary, when an electron "falls" from an orbit of higher quantum number to one of lower quantum number, the atom gives out energy.

The model satisfies the experimental requirement that the atom shall exist in stationary states of definite energy. It is not compatible, however, with classical electrodynamics, because the electron does not radiate electromagnetic energy continuously in the course of its circular motion. By analogy with the behaviour first observed in connexion with heat radiation, a new assumption is made in this atomic model, namely, that there is no radiation from those orbits (stationary states) selected by the quantum conditions.

According to BOHR's second postulate (p. 176), the emission of light is due to the transition from a stationary state or permitted orbit of higher energy W_n to another of lower energy W_m, the energy difference $W_n - W_m$ being radiated out in the form of monochromatic light of frequency $\nu = (W_n - W_m)/h$.

Substitution of the values obtained above for W_n and W_m gives the following expression for the wave-number $\bar{\nu}$ or ν/c:

$$\bar{\nu} = R_{\infty} Z^2 \left(\frac{1}{m^2} - \frac{1}{n^2} \right),$$

where $R_{\infty} = 2\pi^2 m e^4/(ch^3)$.

Inserting the numerical values of the quantities involved, we obtain

$$R_{\infty} = 1{\cdot}097 \times 10^5 \text{ cm.}^{-1}.$$

The subscript ∞ is put in to show that the mass of the nucleus is considered to be infinitely great relative to that of the electron.

In the case of hydrogen ($Z = 1$) the above formula gives for the permitted spectral lines the very same frequencies as are given by the empirical generalized BALMER formula (p. 183). The quantitative agreement between the calculated value of the numerical factor R and the observed value encouraged the wider application of the theory, in spite of its break away from classical electrodynamic ideas. Many phenomena found surprisingly simple explanations in the light of the theory, the inception of which marked the beginning of a quite extraordinary development of atomic physics. Even the shortcomings which soon became apparent in the theory could not stop this development, but merely led to suitable improvements and extensions.

Fig. 54 gives a diagrammatic representation of the mechanism underlying the emission of the different lines of the hydrogen spectrum according to the model just described. This is really essentially the same as the diagram of fig. 50, p. 185; the latter has the additional advantage that quantitative information can be read off directly from it.

Nucleus of Finite Mass.—So far the mass M of the nucleus has been assumed to be infinitely great relative to m, that of the electron. If this assumption is dropped and both masses are regarded as finite, then account has to be taken of the fact that the motion of the system takes place about its centre of gravity, which does not coincide with the centre of the nucleus. Both the electron and the nucleus now move in orbits about their common centre of gravity, though on account of its greater mass the nucleus moves only to a relatively small extent. When this effect is taken into account, the formulæ obtained are modified in that the reduced mass $\mu = Mm/(M + m)$ appears in place of m. Thus we obtain

$$R = \frac{2\pi^2 \mu e^4}{ch^3} = \frac{2\pi^2 m e^4}{ch^3\left(1 + \frac{m}{M}\right)} = \frac{R_\infty}{1 + \frac{m}{M}}.$$

The significance of this modification does not lie so much in the small correction which it involves in the value for the RYDBERG constant for hydrogen, since this correction lies within the limits of error of R as calculated in this way (but see later the case of the hydrogen isotope of mass 2). Rather does the significance of the modification become apparent in the application of the expression to the one-electron systems of other elements, a matter which will now be discussed.

Spectra of One-Electron Systems.—The model described above is not restricted to the hydrogen atom, but applies quite generally to all systems in which one electron circulates about a positively-charged nucleus. Such a system is, for example, the helium ion He^+. It has already been shown that the mass of the helium atom is four times that of the hydrogen atom and that its atomic number is $Z = 2$, i.e. that it consists of a nucleus of mass 4 with a double positive charge and two electrons circulating round it. In the ion one electron has been removed, so that we are left with a system consisting of a nucleus of mass 4 with a double positive charge and only one electron circulating round it. Similar one-electron systems are Li^{++}, Be^{+++}, and B^{++++}, the nuclear charges and masses being given by the respective atomic numbers and atomic weights. As can be seen from the formulæ, increase of the nuclear charge Z results in a corresponding decrease in the radii of the permitted orbits and a large displacement of corresponding lines (i.e. lines involving the same quantum numbers n and m) towards shorter wavelengths. Many of the theoretically-predicted lines have actually been found experimentally at exactly the positions required by the calculations. In the case of He^+ the series with the terminal quantum numbers 4 (PICKERING), 3 (FOWLER), 2, and 1 are known. The first two lines of the Li^{++} series with terminal quantum number 1 and the first line of the corresponding series for Be^{+++} have also been observed (EDLEN and ERICSON). The last named lies at $\lambda = 75{\cdot}94$ Å., i.e. on the border of the X-ray region.

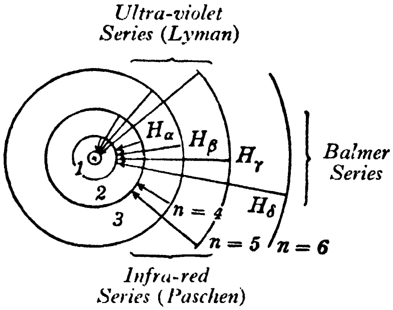

Fig. 54.—Diagram showing the production of the hydrogen lines according to the Bohr model

Every alternate line of the He^+ series

$$\bar{\nu} = 4R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) = R\left[\frac{1}{2^2} - \left(\frac{2}{n}\right)^2\right]$$

coincides with a line of the BALMER series of hydrogen. As we see from the formula, as written above, this coincidence occurs for those He^+ lines for which n is even. For this reason the series in question was previously ascribed to hydrogen and half-integral values ($\frac{1}{2}n$) were used in place of n. The conditions of production prove, however, that the lines are due to helium, and in the following way it was actually found possible to demonstrate that they really do belong to this element. There must be a small difference in the frequencies of the nearly coincident He$^+$ and H lines because of the difference in the Rydberg constant arising from the difference in the nuclear masses. According to the formula given above, the Rydberg constant for hydrogen must be smaller than that for helium, i.e.

$$R_H = \frac{R}{1 + \frac{m}{m_H}} < R_{He} = \frac{R}{1 + \frac{m}{4m_H}}.$$

Hence the frequencies of the He$^+$ lines must be proportionally greater, i.e. the lines must be displaced towards the violet relative to the corresponding H lines. Accurate measurements actually show this displacement, the observed magnitude of which is exactly that predicted by the theory (in the visible about 2 Å.).

Spectroscopic Determination of *e/m* for the Electron.—Since the Rydberg constant R can be determined very accurately from spectroscopic data—the accuracy of measurement being among the highest yet attained in the whole of physics—the result can be used to obtain an accurate value for a quantity involved in R. It is further possible to determine a very accurate value for e/m from spectroscopic determination of R_H and R_{He}. From the formulæ given above,

$$\frac{m}{m_H} = \frac{R_{He} - R_H}{R_H - \frac{1}{4}R_{He}}.$$

Again, the quantity e/m_H (the electro-chemical equivalent charge or faraday (Vol. III, p. 157)) is very accurately known. From these data the value of e/m can be determined very precisely, using the equation

$$\frac{e}{m} = \frac{e}{m_H} \div \frac{m}{m_H}.$$

With $R_H = 109{,}677{\cdot}759 \pm 0{\cdot}008$ cm.$^{-1}$ and $R_{He} = 109{,}722{\cdot}403 \pm 0{\cdot}004$ cm.$^{-1}$ we obtain

$$\frac{e}{m} = (1{\cdot}761 \pm 0{\cdot}001) \times 10^8 \text{ coulombs/gm.}$$

(cf. Vol. III, p. 321).

Continuous Spectra beyond Series Limits.—Regions of continuous spectral emission are observed on the short-wave side of the limits of the Balmer and Lyman series. These are due to the existence of states of higher energy than that corresponding to an infinitely large quantum number. In terms of the model these energy states are represented by electrons moving in parabolic or hyperbolic orbits. Electrons with excess kinetic energy approach the nucleus, curve round it once, and then fly off again. Since these motions are not periodic they are not quantized, but form a continuous range of energy values. If such an electron is captured by the ion in the encounter, its final state must be a stationary one, i.e. it must take up a quantized orbit. The excess energy which the electron possessed before being captured is radiated as monochromatic light; but since all energy states above that of quantum number $n = \infty$ are possible, the observed spectrum is the additive result of many such emissions, i.e. is a continuous spectrum extending towards shorter wave-lengths from the limit of that series whose constant term corresponds to the quantum state in which the electron is captured.

The Correspondence Principle.—According to MAXWELL's electrodynamics, an electron moving in a circular orbit would necessarily radiate an electromagnetic wave whose frequency would be identical with the orbital frequency (Vol. III, p. 622). We may write this "classical" frequency as $\nu_{\text{cl.}} = 1/\tau$, where τ is the periodic time of the orbital motion. In the BOHR atomic model the frequency emitted is not connected in this way with an actual orbital frequency, but with the energy difference between stationary states. But we know that the laws of classical electrodynamics are satisfactorily obeyed in the case of long electromagnetic waves (say from $\lambda = 0{\cdot}01$ mm. upwards). Hence it is to be expected that if the BOHR atomic model really does represent the essential features of the behaviour of atoms, it will approximate to the classical model for these relatively low frequencies. This, indeed, is actually the case.

For transitions between quantum numbers which are relatively very high (e.g. 21 and 20) the emitted frequency coincides very nearly with the actual frequencies of rotation of the electron in these orbits. If $\nu = \bar{\nu}c$ is the frequency in sec.$^{-1}$, we may write

$$\nu = cRZ^2\left(\frac{1}{n^2} - \frac{1}{(n+\Delta n)^2}\right) = cRZ^2\,\frac{(2n+\Delta n)\Delta n}{n^2(n+\Delta n)^2}.$$

Where Δn is small compared with n (e.g. 1 compared with 20), we have approximately

$$\nu \sim cRZ^2\,\frac{2\Delta n}{n^3},$$

or if $\Delta n = 1$,

$$\nu \sim \frac{2cRZ^2}{n^3}.$$

Now according to p. 191

$$\frac{1}{\tau} = \frac{4\pi^2 mZ^2e^4}{n^3h^3} = \frac{2RcZ^2}{n^3}.$$

But $1/\tau = \nu_{\text{cl.}}$, so that we have $\nu \sim \nu_{\text{cl.}}$. For high quantum numbers, therefore, the frequency of the light emitted when there is a change of unity in the quantum number asymptotically tends to the frequency of rotation of the electron in the orbits concerned. If $\Delta n > 1$, but Δn still $\ll n$, then

$$\nu \sim \frac{2RcZ^2}{n^3}\,\Delta n = \nu_{\text{cl.}}\,\Delta n,$$

i.e. in the region of very high quantum numbers the quantum transitions in which the quantum number changes by several units correspond to the respective overtones or harmonics of the orbital frequency of the electron.

From this analogy BOHR drew a very important conclusion, known as the *correspondence principle*, which was of great importance in the early stages of the development of the theory of atomic structure. It may be expressed as follows: *For large quantum numbers* n *the behaviour of the atom asymptotically tends to that which would be expected on the basis of classical electrodynamics.* For large quantum numbers, therefore, it is possible to calculate the intensities and polarizations of the emitted radiation—properties about which the atomic model, as hitherto described, tells us nothing. For smaller quantum numbers these calculations remain approximately valid, i.e. the classically-computed data on intensity and polarization can be transferred approximately to the corresponding lines given by the atomic model.

Thus the correspondence principle is only an approximate rule, and it involves many indeterminacies which cannot be discussed here. The problem of the direct calculation of the intensity and polarization of the light emitted by an atom was first solved in a different way (p. 272); but the correspondence principle was of very great service in the development of the theory. In particular, it enables us to predict with certainty which transitions are forbidden, i.e. it leads to certain **selection rules,** as required by experiment (p. 180). Actually the following general rule is found to hold: *A spectral line is forbidden in emission if the corresponding harmonic component does not occur in the Fourier series of the classical periodic process.* Some examples will be dealt with later (p. 204).

An important consequence of this may be pointed out here. The periodic process, as far as we have hitherto treated it, is a circular orbital motion, the orbit being given by $x = a\cos 2\pi\nu_{\mathrm{cl.}}t$, $y = a\sin 2\pi\nu_{\mathrm{cl.}}t$, where $\nu_{\mathrm{cl.}} = 1/\tau$. The emitted spectrum consists of the fundamental only; the amplitudes of all the harmonics 2ν, 3ν, . . . are zero. As seen by an observer in the z-direction, the light is circularly polarized. Now the transitions $\Delta n > 1$ correspond, as was noted above, to the harmonics of the transition $\Delta n = 1$. These harmonics are absent in the case of the circular orbit, and we must therefore conclude that quantum transitions with $\Delta n > 1$ are forbidden when the orbits are circular. Actually, however, transitions with $\Delta n > 1$ are observed as the higher members of series. This must mean that our atomic model is too simple and requires modification. The necessary modification may be introduced by allowing elliptic orbits for the electron. The periodic processes in the x- and y-directions can then be analysed into Fourier series (Vol. II, p. 223), namely

$$x = a\cos 2\pi\nu t + a'\cos 4\pi\nu t + a''\cos 6\pi\nu t + \dots$$
$$y = b\sin 2\pi\nu t + b'\sin 4\pi\nu t + b''\sin 6\pi\nu t + \dots$$

Thus all the harmonics are present as harmonic components. Hence by the correspondence principle all transitions between elliptic orbits are permitted, though of course with different probabilities. We must therefore go on to consider this modified atomic model.

Atomic Model with Elliptic Orbits.—From the existence of sharp spectral lines it is obvious from the start that the same quantization must hold for elliptic orbits as for circular orbits, i.e. only certain ellipses (stationary states) out of the continuous range to be expected on classical principles are possible. We have accordingly to find the quantum conditions.

An ellipse is determined by two parameters, e.g. by its major and minor axes a and b respectively. Thus we have a system with two degrees of freedom and must therefore consider two phase integrals (see p. 188). It is convenient to introduce polar co-ordinates, i.e. to characterize each point on the orbit by means of (i) the magnitude of the radius vector to it from the focus, and (ii) the azimuthal angle φ described by this radius relative to some zero position. The quantum conditions can then be written:

$$\oint p_\phi d\varphi = n_\phi h \quad \text{and} \quad \oint p_r dr = n_r h$$

(see p. 188). Thus we resolve the motion into two periodic motions, a non-uniform circular motion and a non-harmonic oscillation along the radius vector.* The motion is completely analogous to that of a planet in its orbit. According to the theorem of equal areas for central orbits (Vol. I, pp. 51 and 174), the angular momentum p_ϕ is constant, i.e. $p_\phi = mr^2 d\varphi/dt = \text{const.}$ Hence the value of the phase integral is given by

$$p_\phi \oint d\varphi = 2\pi p_\phi = n_\phi h.$$

The radial momentum, $p_r = m\,dr/dt$, is not constant, and the phase integral can only be calculated by more complicated methods. The result obtained is

$$\oint p_r dr = 2\pi p_\phi \left(\frac{1}{\sqrt{1-\varepsilon^2}} - 1\right) = n_r h,$$

where ε is the numerical eccentricity of the ellipse. Putting $n_\phi + n_r = n$, we obtain the value

$$\varepsilon = \sqrt{1 - \frac{n_\phi^2}{n^2}}$$

from the above equation.

The orbit with $n_\phi = 0$, for which the electron would oscillate on a straight line through the nucleus, is here excluded as having no physical meaning. Hence n_ϕ can only assume the values 1 to n, while n_r can only assume the values 0 to $(n - 1)$ (see p. 267). The sum of n_ϕ and n_r, i.e. n, is called the *principal quantum number*.

We are particularly interested in the shapes of the permitted ellipses and the energies of the atom in the corresponding stationary states. We may proceed in essentially the same manner as for circular orbits. At every point of an orbit there must be equilibrium between the electrical force of attraction and the centrifugal force. In particular we consider aphelion (i.e. the position of greatest distance from the nucleus), distinguishing the quantities relating to this point by the subscript A. We have

$$\frac{mv_A^2}{\rho_A} = \frac{Ze^2}{r_A^2},$$

---

* The two quantum numbers n_ϕ and n_r are often referred to as the *azimuthal* and *radial quantum number* respectively.

where ρ_A is the radius of curvature of the orbit at the point A. Now for an ellipse it can be shown that

$$\rho_A = \frac{b^2}{a} = a(1-\varepsilon^2)$$

and that

$$r_A = a(1+\varepsilon).$$

Hence we may write

$$\frac{mv_A^2}{a(1-\varepsilon^2)} = \frac{Ze^2}{a^2(1+\varepsilon)^2}. \quad \ldots\ldots\ldots \quad \text{(i)}$$

As in the case of circular orbits, we must also apply the quantum conditions. We have seen above that one of these may be written

$$2\pi p_\phi = n_\phi h.$$

Since p_ϕ is constant, we may substitute in this the value for aphelion, i.e. $mr_A^2 d\varphi_A/dt$. Now the element of angle $d\varphi$ is equal to ds/r, where ds is the corresponding element of arc on the orbit. Hence we have

$$\frac{d\varphi_A}{dt} = \frac{1}{r_A}\frac{ds_A}{dt} = \frac{1}{r_A}v_A.$$

The value of p_ϕ at aphelion is therefore $mr_A^2 v_A/r_A = mr_A v_A$, and the quantum condition above becomes

$$2\pi m r_A v_A = n_\phi h.$$

Substituting $r_A = a(1+\varepsilon)$, we obtain

$$2\pi ma(1+\varepsilon)v_A = n_\phi h,$$

which is an expression involving both the quantum numbers n_ϕ and n_r, since ε contains n_r. Squaring and substituting the value of v_A^2 from equation (i) at once gives

$$a = \frac{h^2 n_\phi^2}{4\pi^2 mZe^2(1-\varepsilon^2)},$$

whence, by substituting the value of $(1-\varepsilon^2)$ from above, we have

$$a = \frac{h^2}{4\pi^2 mZe^2} n^2.$$

Utilizing the relation $b^2 = a^2(1-\varepsilon^2)$, we obtain

$$b = a\frac{n_\phi}{n}.$$

To calculate the total energy W we may again use the values at aphelion, since W is constant. We have

$$W = E_{\text{kin.}} + E_{\text{pot.}} = \tfrac{1}{2}mv_A^2 - \frac{Ze^2}{r_A},$$

which, if we substitute the values of v_A^2 and r_A, becomes

$$W = \frac{m}{2}\frac{Ze^2(1-\varepsilon^2)}{ma(1+\varepsilon)^2} - \frac{Ze^2}{a(1+\varepsilon)} = -\frac{Ze^2}{2a}.$$

Inserting the value obtained above for a, we finally obtain

$$W = -\frac{2\pi^2 mZ^2e^4}{h^2}\cdot\frac{1}{n^2}.$$

An exactly similar calculation to that given on p. 191 for circular orbits shows that the wave-number of the light emitted when a transition between two stationary states takes place is given by the formula

$$\tilde{\nu} = RZ^2\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

where the constant R has the same value as before. The important point of this discussion is that the total energy of a permitted elliptic orbit is determined solely by the principal quantum number and is equal to the energy of the corresponding circular orbit. Thus all ellipses with the same principal quantum number have the *same* energy, no matter what their shape is. According to the model, therefore, a given spectral line may be produced by a number of different but equivalent transitions, between which the model (as hitherto considered) gives no means of distinguishing. Although the system possesses two degrees of freedom, *one* quantum number suffices to determine the permitted energies. Such a system is said to be **degenerate.** The degeneracy is removed, i.e. the previously equivalent states become distinguishable and different as regards energy, when external electric or magnetic fields are superimposed upon the Coulomb field. In the case of complicated atoms the internal atomic field may suffice. Under these circumstances the lines emitted by different transitions between the same principal quantum numbers no longer coincide.

It is a matter of importance for subsequent work to consider in more detail the different types of orbit which correspond to a given principal quantum number. We have $n = n_\phi + n_r$, the case $n_\phi = 0$ being excluded (see above). It follows at once from the eccentricity formula above that when $n_r = 0$, i.e. $n = n_\phi$, the orbit is circular. For uniformity with the customary spectroscopic notation (the justification of which will become apparent on p. 267), it is convenient to use the quantity $l = n_\phi - 1$ instead of n_ϕ. This number l, like n_r, can assume all values from 0 up to $(n - 1)$. The numbers l, n_r, and n are connected by the formula

$$l + n_r = n - 1.$$

The possible values of l, n_r, and the major and minor axes of the elliptic orbits corresponding to different principal quantum numbers n, are therefore as follows:

n	l	n_r	a	b
1	0	0	a_1	a_1
2	0	1	$4a_1$	$2a_1$
	1	0	$4a_1$	$4a_1$
3	0	2	$9a_1$	$3a_1$
	1	1	$9a_1$	$6a_1$
	2	0	$9a_1$	$9a_1$
4	0	3	$16a_1$	$4a_1$
	1	2	$16a_1$	$8a_1$
	2	1	$16a_1$	$12a_1$
	3	0	$16a_1$	$16a_1$

The ellipses are drawn to scale in fig. 55. The numbers attached to the different orbits give the corresponding values of n and l. Thus 3_1 means $n = 3$, $l = 1$.

We see that the orbits with $l = 0$ differ most from circles. Hence it is for these orbits that we shall expect external fields to have their greatest effect in splitting up energy states which are otherwise indistinguishable.

Effect of the Variability of the Mass of the Electron.—For elliptic orbits, as for circular orbits, we have seen that the energy depends upon one quantum number, the principal quantum number. According to this every transition between two given principal quantum numbers must correspond to the same energy (i.e. must give emitted light of the same frequency), no matter what the shapes of the orbits. Actually, however, experiment shows that the lines of the hydrogen spectrum are not simple, but consist of assemblages of very close components; they are said to possess a *fine structure* (compare Vol. IV, pp. 194, 197 also Plate XV, facing p. 196). Fig. 56 shows the fine structure of the line arising from the transition $\tilde{\nu} = 4R\left(\frac{1}{3^2} - \frac{1}{4^2}\right)$ for the helium ion He^+, which is also a one-electron system with the same model as H. The model, as hitherto considered, is thus unable to account for all the features experimentally observed. This is presumably due to the simplifying assumptions which have been made. One of these assumptions is that the mass of the electron is constant. It has been experimentally shown that the mass of the electron increases with increasing velocity (Vol. III, p. 322, and this volume, p. 227). Now of all the orbits with a given principal quantum number the circular orbit has the greatest circumference. Since the time of revolution is the same for all the orbits with a given value of n, the average velocity of the electron, and hence its average mass, must be greatest for the circular orbit. This variability of mass may be expected to affect the energy values of the variously-shaped orbits, and calculation shows that this is actually the case. If W_0 is the energy obtained without taking account of the variability

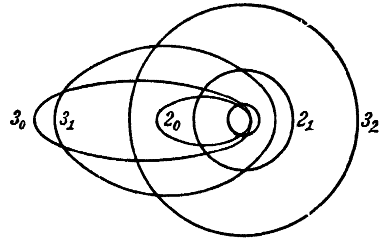

Fig. 55.—Elliptic orbits for a one-electron system

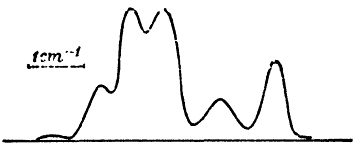

Fig. 56.—Fine structure of the He+ line 4686 Å. (after Paschen)

of mass, the value W obtained when due account is taken of it was proved by Sommerfeld to be

$$W = W_0\left[1 + \frac{a^2Z^2}{n^2}\left(\frac{n}{n_\phi} - \frac{3}{4}\right)\right],$$

where a, the *fine structure constant*, is the velocity in the first BOHR circle expressed as a fraction of the velocity of light, i.e. $a = 2\pi e^2/(hc)$. Thus the degeneracy is removed by the variability of the mass of the electron: W is no longer determined solely by n. In the elliptic orbits the change of mass of the electron with velocity is particularly evident where the velocity is greatest, i.e. in perihelion (the position of closest approach to the nucleus). The result is that the electron does not retrace exactly the same orbit at each successive revolution, but moves in a rosette (see fig. 57). By what has been said above, the term displacement arising from the variability in the mass of the electron is given (in cm.$^{-1}$) by

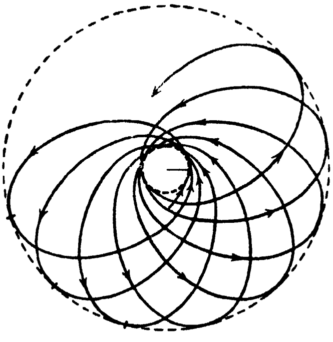

Fig. 57.—Effect of the variation of the mass of the electron with velocity upon the nature of the orbit.

$$\Delta T = Ra^2\left(\frac{Z}{n}\right)^4\left(\frac{n}{n_\phi} - \frac{3}{4}\right) = 5{\cdot}82\left(\frac{Z}{n}\right)^4\left(\frac{n}{n_\phi} - \frac{3}{4}\right)\text{cm.}^{-1}.$$

For hydrogen the effect is of the order of magnitude of fractions of 1 cm.$^{-1}$, but it increases very rapidly as Z increases.

It is found that this refinement of the model does actually account for experimental observations. But the model still has defects. These are to a large extent removed by the introduction of the idea of electron spin (see pp. 210, 312). The theory of the electron which is most widely accepted at present is that due to Dirac, whose treatment takes account of the theory of relativity.

Spatial Orientation of the Electron Orbits.—If a special direction is fixed in space, e.g. by the application of an external electric or magnetic field, the energy of the individual orbits depends on their inclination to the direction of the field as well as on the strength of the field. Experiment shows that in these cases (STARK and ZEEMAN effects) there is a splitting up of the emitted spectral lines into a number of sharply-defined monochromatic components. From this we must conclude that there is a quantum condition which permits only certain discrete orientations relative to the field-direction out of the continuous range to be expected from classical considerations.

Hence for the solution of this problem we require three quantum numbers, corresponding to the three degrees of freedom of the system in space. To begin with we shall assume that the external field is extremely weak, so that it may merely serve to fix a special direction in space without appreciably altering the energy values of the system. The motion therefore is confined to one plane, and the orbit is an ellipse, as before.

The position of the orbital electron in space may be expressed by means of the three-dimensional polar co-ordinates r, θ, and ψ (radius, colatitude, and longitude respectively). Hence there are three phase integrals and three quantum conditions to be fulfilled, namely

$$\oint p_\theta d\theta = n_t h; \quad \oint p_\psi d\psi = n_\psi h; \quad \oint p_r dr = n_r h.$$

Of these the radial phase integral is identical with the corresponding integral for the plane problem, provided that (as is assumed here) the external force is sufficiently small. In plane polar co-ordinates the kinetic energy is (p. 197)

$$E_{\text{kin.}} = \frac{1}{2}\left(p_r \frac{dr}{dt} + p_\phi \frac{d\varphi}{dt}\right).$$

Since the energy is assumed to be unaltered by the external field, this must be equal to the kinetic energy expressed in the spatial co-ordinates, namely

$$E_{\text{kin.}} = \frac{1}{2}\left(p_r \frac{dr}{dt} + p_\psi \frac{d\psi}{dt} + p_\theta \frac{d\theta}{dt}\right).$$

From this it follows that

$$p_\phi d\varphi = p_\psi d\psi + p_\theta d\theta,$$

and the same holds for the integrals. Hence

$$n_\phi = n_\psi + n_\theta.$$

The quantity p_ψ is the angular momentum about the direction of the field and must be constant for a stationary state. Hence the corresponding quantum condition on integration becomes

$$p_\psi = n_\psi \frac{h}{2\pi}.$$

This angular momentum p_ψ may be represented as a vector of corresponding length in the direction of the field. Similarly, the total angular momentum p_ϕ may be represented as a vector of magnitude $p_\phi = mr^2\omega = j\frac{h}{2\pi}$ normal to the plane of the orbit (see fig. 58). Then p_ψ is equal to the resolved part of p_ϕ along the direction of the field, i.e.

$$p_\psi = p_\phi \cos\alpha,$$

where α is the angle between the direction of the field and the normal to the plane of the orbit. Hence the above quantum condition can be formulated as follows: *the resolved part of the resultant or total angular momentum in the direction of the field must be an integral multiple of $h/(2\pi)$.*

The result derived from the model is therefore as follows: *the plane of the orbit can only set itself at certain definite angles to the special direction in space fixed by the field. These permitted angles are such that the* *projection of the total angular momentum on the field direction is an integral multiple of $h/(2\pi)$.*

The total angular momentum is itself an integral multiple of $h/(2\pi)$, being given by a quantum number which we may call j. Fig. 59 shows that the projection of a vector of integral magnitude j on the field direction may assume the integral values $+j$, $(j-1)$, $(j-2)\ldots(2-j)$, $(1-j)$, $-j$, i.e. altogether $(2j+1)$ different values. Hence a total angular momentum determined by the integral quantum number j may take up $(2j+1)$ permitted orientations relative to the direction of the field.

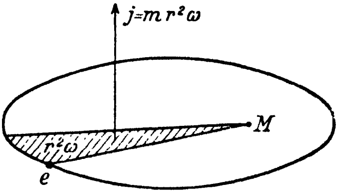

Fig. 58.—Vectorial representation ot orbital angular momentum

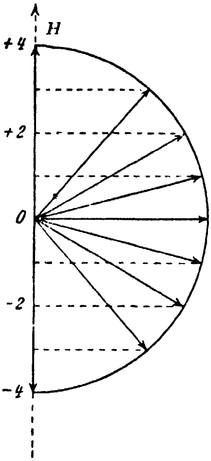

Fig. 59.—Integral projections of an integral vector ($j = 4$).

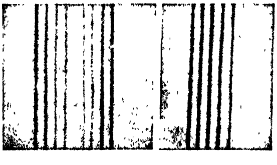

Fig. 60.—Zeeman splitting of the 4269·4 Å. line of tungsten in a magnetic field; on the left the s-components, on the right the p-components. The central line of the p-components coincides with the undisplaced line.

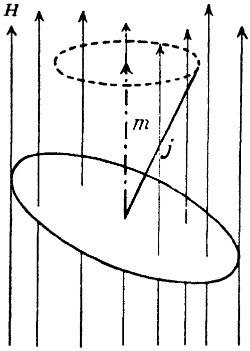

Fig. 61.—Larmor precession in a magnetic field

The Atomic Model in a Magnetic Field (Zeeman Effect).—As an example of an external field we shall first consider a weak uniform magnetic field. When such a field is applied to a source of light, it is observed that the previously simple lines of the emitted spectrum are split up into several close components (Zeeman, 1896). Fig. 60 shows photographs of the Zeeman effect.

The explanation of this behaviour is as follows. According to LARMOR, the effect of a uniform magnetic field on the plane electron orbit (see Vol. III, p. 448) is to cause the plane of the orbit to precess (Vol. I, p. 158) about the direction of the field, so that the normal to the plane of the orbit describes the curved surface of a cone with its axis in the direction of the field (see fig. 61). To an observer looking in the direction and sense of the lines of force, the sense of precession appears clockwise. The frequency of the LARMOR precession is (if we write μ for the mass of the electron)

$$\nu_L = \frac{e}{\mu}\frac{H}{4\pi c};$$

if H is expressed in gausses, the corresponding wave-number (in cm.$^{-1}$) is found to be $\bar{\nu}_L = 4{\cdot}70 \times 10^{-5}$ H.

If H has a finite value, there will be a change in the kinetic energy of the orbital motion. This change is given (DEBYE, SOMMERFELD, 1916) by $\Delta E = mh\nu_L$, where m stands for the possible values of n_ψ.

Consider two states with the quantum numbers n and n'. In the absence of the field their energies are E_n and $E_{n'}$ and the frequency emitted by a transition between them is given by $h\nu = E_n - E_{n'}$. In presence of the field the energies become respectively $(E_n + mh\nu_L)$ and $(E_{n'} + m'h\nu_L)$, and the emitted frequency ν_H is given by $h\nu_H = E_n + mh\nu_L - E_n - m'h\nu_L$. Hence the change of frequency caused by the field is $\Delta\nu = \nu_H - \nu = (m - m')\nu_L$. If the maximum possible magnitudes of m and m' are respectively j and j', we may expect to find a pattern of spectrum lines with the following frequency displacements relative to the field-free line: 0, $\pm\nu_L$, $\pm 2\nu_L, \ldots \pm(j + j')\nu_L$.

In actual fact, however, experiment shows that the whole array of lines does not always appear, but that often only the field-free line and the two components $\pm\nu_L$ are observed (the so-called normal ZEEMAN effect). The reason for this can be derived (see below) by an argument based on the correspondence principle.

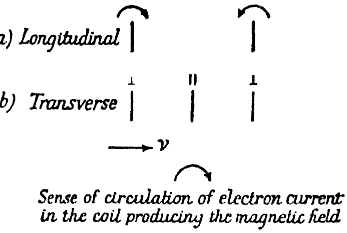
(a) Longitudinal
(b) Transverse
⊥
∥
⊥
ν
Sense of circulation of electron current in the coil producing the magnetic field

Fig. 62.—States of polarization in the "normal" Zeeman effect

The three lines just mentioned only occur when the direction of observation is at right angles to that of the lines of force (so-called *transverse effect*). In this case the outer components are polarized in such a way that their electric vector is normal to the lines of force (so-called *s*-components), while the electric vector of the central undisplaced line is parallel to the lines of force (so-called *p*-polarization). When the effect is observed along the direction of the lines of force (so-called *longitudinal effect*), the undisplaced line is completely absent. Only the two displaced components appear, and they are circularly polarized in opposite senses, the longer-wave component being circularly polarized in the same sense as that of the circulation of the electrons in the coil which is used to produce the magnetic field. These states of polarization are represented diagrammatically in fig. 62.

Some account of the observed phenomena can be given even on a classical basis, in particular the polarization of the lines. If the atom is regarded

as a source of electromagnetic waves, the motions of electric charges to which these waves are due may be resolved into two components, parallel and perpendicular to the direction of the field. The field has no effect on the component which is parallel to its own direction. Now an electric oscillator does not radiate in the direction of its own oscillation (Vol. III, p. 626). Hence it follows that the undisplaced line must be missing from the spectrum as viewed along the lines of force (longitudinal effect). This line must be visible, however, if the spectrum is viewed normally to the field direction (transverse effect) and must be plane-polarized with its electric vector parallel to the direction of the field. These conclusions are in agreement with experiment. The direction of the field may be taken as the z-direction, so that the plane normal to it is the xy-plane. In consequence of the Larmor precession a precessional frequency is superimposed upon the x- and y-components. The states of polarization of the corresponding lines can be deduced by considerations similar to those given above. The fact that only three Zeeman components appear, instead of the $2(j+j')$ which would at first sight be expected, can be accounted for in the following way. The z-component of the electromagnetic "transmitter" (i.e. the oscillation in the direction of the lines of force of the field) contains, as explained above, only the undisplaced frequency. Hence, since no Fourier components involving ν_L occur in this oscillation, the corresponding quantum number m must remain constant for all transitions for which the light is polarized with its electric vector parallel to the direction of the field, i.e. for the p-components we must have $\Delta m = 0$. In the x- and y-directions, on the other hand, the precessional frequency ν_L is superimposed, so that the corresponding Fourier series contain the term $2\pi\nu_L t$. The coefficients of this term are $+1$ and -1; for only in very intense fields need account be taken of the harmonics. Hence only the frequencies $\pm\nu_L$ enter into the Zeeman effect, or, in other words, the quantum number m can only change by ± 1 for the components which are polarized with their electric vector at right angles to the direction of the field. Thus for the s-components we must have $\Delta m = \pm 1$.

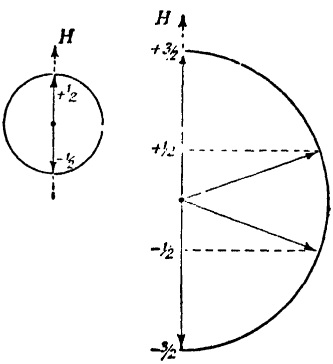

Fig. 63.—Possible orientations of a half-integral vector ($j = \frac{1}{2}$ and $j = \frac{3}{2}$) so as to give projections with integral differences.

Fig. 63 shows the possible inclinations of a half-integral vector j ($j = \frac{1}{2}$ and $j = \frac{3}{2}$) such that its projections upon the special direction fixed by an external field differ by integral amounts (compare fig. 59, p. 203). As will be seen later, these cases are also of importance.

The Stern-Gerlach Experiment.—In 1921 Gerlach and Stern carried out experimental investigations into the way in which free atoms orient themselves in a magnetic field. The underlying idea is that of shooting a sharply-bounded beam of atoms through a non-uniform magnetic field (fig. 64). Since each atom contains circulating electric charges, it must have a definite resultant magnetic moment. In certain cases the magnetic moments due to the different electron orbits may balance one another so as to give a zero resultant. When an atom of magnetic moment μ comes into the magnetic field, the plane of its electronic orbit (or, more accurately, the angular momentum vector j to which its magnetic moment is due) must orient itself relative to the direction of the field in the manner discussed above. If the field is non-uniform (as in the STERN-GERLACH experiment), there will be a resultant force on the atom of magnitude $P = \mu \frac{\partial H}{\partial s} \cos \alpha$, where s is the distance measured along the lines of force and α is the angle between the lines of force and the magnetic moment μ (cf. Vol. III, p. 431). If every orientation is permitted, then P will be able to assume every value between $\pm \mu \frac{\partial H}{\partial s}$. Those atoms whose orbital planes are in the direction of the lines of force of the field (or, better, whose total angular momentum vector j is normal to the lines of force) will experience no force ($\cos \alpha = 0$) and will fly through the field undeflected. On the contrary, those whose j-vector is parallel to the lines of force will experience the maximum force ($\cos \alpha = 1$). Moreover, the sense of this force will be either positive or negative, according as the j-vector is set so that its sense is the same as that of the lines of force or opposed to it (so-called parallel and antiparallel orientations). If all the intermediate orientations are also possible (in which case, according to our model, the orbital planes will precess about the line of the field), the initially sharply-bounded atomic beam will be diffusely broadened after passing through the non-uniform field. If, on the other hand, only a certain number of definite orientations are permitted, then the force P can only assume certain definite values and the beam after passage through the field will be found to be split up into a corresponding number of sharp component beams. The actual form of the beam can be made visible by receiving it upon a plate and then suitably treating the trace so obtained.

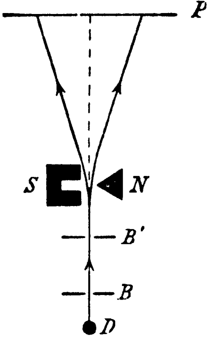

Fig. 64.—Diagram of the experimental apparatus for investigating the spatial orientation of atoms in a magnetic field. D, source of atoms; B, B', screens with apertures; P, plate on which trace is received.

The atomic rays are produced by the method described in Vol. II, p. 53. The non-uniform magnetic field can be produced by using a wedge and a grooved block as pole-pieces (see fig. 64). The treatment of the trace of the beam varies according to the kind of atoms used. Silver atoms can be caught upon cooled glass and then rendered visible by development. The quantities directly deposited are too small to be clearly seen. Hydrogen atoms are allowed to impinge upon a glass plate covered with molybdenum oxide. The oxide is thereby reduced and the trace becomes visible on account of the blue colour produced.

Calculation shows that each atom moves in a parabola. The deflection d of the atom leaving the field region is found to be

$$d = \tfrac{1}{2}\mu \frac{\partial H}{\partial s} \cos\alpha \frac{l^2}{mv^2},$$

where l is the distance traversed in the field and m and v are the mass and the velocity of the atom respectively. The field gradient $\partial H/\partial s$ can be measured by means of the change of resistance of a bismuth wire placed in the direction of the atomic beam (see Vol. III, p. 247). Hence the formula gives the value of $\mu \cos\alpha$, since all the other quantities involved are measurable. A certain diffuseness is unavoidable owing to the velocity distribution of the atoms; but the magnetic splitting can be made relatively so great that this is of secondary importance.

The STERN-GERLACH experiment yields the remarkable result that the initially sharply-bounded atomic beam is split up by the non-uniform magnetic field into distinct components. According to what has been said above, this can only mean that the atoms must take up certain definite orientations relative to the direction of the field. Figs. 65 and 66 show reproductions of the first exposures, which were made with beams of silver atoms. In fig. 65 the magnetic field is off. In fig. 66, taken under similar conditions except that the field is switched on, the central region is completely free from atoms, the trace being split into two more or less sharp components. At the top and bottom the lines run together owing to the decrease of the variation of the field towards these edges. The irregularities in the trace near the middle (projection towards the side) are due to the great variation of the field in the immediate neighbourhood of the wedge-shaped pole-

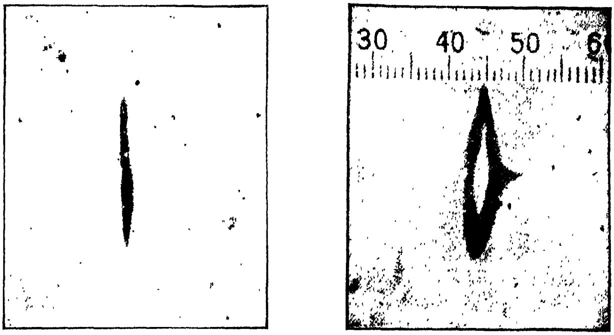

Fig. 65 Fig. 66

Figs. 65 and 66.—Results of the experiment of Stern and Gerlach on the spatial orientation of silver atoms in a magnetic field. On the left is the trace with the field off; on the right the trace with the field on.

[From Sommerfeld, *Atombau und Spektrallinien* (Vieweg, Brunswick).]

piece. In the original the separation of the components amounted to 0·1–0·15 mm. The traces of figs. 65 and 66 lead to the conclusion that the silver atoms must set themselves parallel and antiparallel to the field (i.e. $\cos\alpha = +1$ and -1) and that no other orientations are possible.

The Magneton.—The total mechanical angular momentum p of an electron circulating in an orbit is related to the magnetic moment μ of the corresponding circulatory current by the equation (with e in electromagnetic units)

$$\mu = \frac{ep}{2m},$$

which follows from ordinary electrodynamics (Vol. III, p. 445). Now in atoms p is quantized: $p = jh/(2\pi)$. The magnetic moment μ_1 corresponding to $j = 1$ is given by

$$\mu_1 = \frac{eh}{4\pi m},$$

and therefore involves fundamental constants only. The value of μ_1, which is called the *magneton* (more precisely, the BOHR magneton), is $\mu_1 = 9{\cdot}23 \times 10^{-21}$ gauss-cm. Frequent use is made of the corresponding quantity M_B referred to the gramme-atom or gramme-molecule instead of to the single atom. The two are related by the equation $M_B = \mu_1 N = 5564$ gauss-cm., where N is Avogadro's number.

Substitution of $|\cos\alpha| = 1$ in the results of the Stern-Gerlach experiment gives a value for μ within 10 per cent of the value calculated above for μ_1. This proves that the quantity μ_1 really has a practical significance and that the magnetic moment of the silver atom is one magneton. We shall see later, however, that the magnetic moments of atoms are *not* always integral multiples of the magneton. The actual numerical values involve fractions lying between 0 and 2 and representing the ratios of integers (usually not very large) which can be determined from the structure of the atom. A more detailed account of the problem will be given on p. 317.

Since the silver atom has a very complicated structure, the considerations so far advanced do not enable us to draw any further conclusions from the experimental results just described (but see later, p. 346). Special interest attaches, therefore, to the experiments on beams of hydrogen atoms (WREDE, PHIPPS, and TAYLOR, 1927). Fig. 67 shows the result obtained. The slanting line on the right is the trace obtained in the absence of a magnetic field, while the double line to the left is the corresponding trace with the field on, the plate having been turned between the two exposures. The effect is the same as for silver atoms, namely, two lines displaced in opposite senses and no undisplaced line. Hence it follows that the hydrogen atoms must set themselves with the vector of their magnetic moment either parallel or antiparallel to the field. The value of the magnetic moment, as deduced from the observed effect, is found to be one magneton (within about 10 per cent).

Fig. 67.—Orientation of hydrogen atoms in a magnetic field

[From *Zeitschrift fur Physik*, 1927 (Springer, Berlin).]

This result is at variance with the deductions made above from the atomic model. The ground state of the hydrogen atom has the quantum number $n = 1$, and hence, according to fig. 59, p. 203, we should expect three possible orientations—the two actually observed, and in addition the orientation with $m = 0$ (i.e. the undisplaced beam). The non-appearance of an undisplaced line proves that the angular momentum of the electron in its orbit is not determined by the quantum number n of the model. This is the reason why the special symbol j has been introduced for the quantum number involved.

What value of j is compatible with only two possible projections upon the field direction, the parallel and the antiparallel? If we hold to the rule (based upon experimental results) that the *differences* between the projections of the total angular momentum on the direction of the field must be *integral*, then we are led to assume *half-integral* values of j and the exclusion of the orientation in which j is at right angles to the field (i.e. in which $m = 0$ and the beam is undisplaced). The consequences of these assumptions for the cases $j = \frac{1}{2}$ and $j = \frac{3}{2}$ are shown in fig. 63, p. 205.

Thus the experimental results lead to the conclusion that the total angular momentum is not an integral multiple of $h/(2\pi)$, but on the contrary exceeds this by $\frac{1}{2}h/(2\pi)$. Hence it is necessary to add to our atomic model an angular motion with the angular momentum $\frac{1}{2}h/(2\pi)$. As was suggested in 1925 by UHLENBECK and GOUDSMIT on the basis of other experimental data to be discussed below (p. 312), this motion can only be an internal motion of the electron itself. An intrinsic spinning motion of the electron was assumed by J. STARK in order to explain the process of light emission. The above experiments, like those treated in Vol. III, p. 444 and others to be discussed later, indicate that an angular momentum of $\frac{1}{2}h/(2\pi)$ must be ascribed to the electron. Since this rotatory motion of the electron (so-called *electron spin*) represents a circulation of electricity, it must be associated with a magnetic moment. According to the experiments described above and others to be discussed later (p. 318), this magnetic moment is exactly one Bohr magneton.

Now the magnetic moment of the hydrogen atom deduced from the experimental result of fig. 67 is only *one* magneton. According to the atomic model adopted hitherto, this moment is due to the orbital motion of the electron. In view of the undoubted existence of the spin-moment, we should expect a total moment of two magnetons or zero, according to the orientation. Experiment, however, shows that the atom possesses a moment of *one* magneton—a result which leads to the conclusion that the orbital motion of the electron in the ground state must confer *no* moment upon the hydrogen atom, i.e. must have no orbital angular momentum. This conclusion, however, is quite incompatible with the model we have set up.

Shortcomings of the Bohr Atomic Model.—We see, therefore, that the model hitherto adopted is incapable of providing a satisfactory explanation of observed facts. It is not possible to incorporate in it the spin of the electron, which is required by independent data; for over and above the energy changes due to the variability of the electronic mass, which gives a good explanation of the fine structure of the hydrogen lines, the addition of the electron spin brings other energy changes which are not in agreement with experiment. A solution of this contradiction is not possible in terms of the Bohr atomic model.

There are also other experiments which indicate that in the ground state the structure of the hydrogen atom must be different from that pictured above—that it must, as in fact we were led to conclude, be *without* vectorial orbital angular momentum.

The question whether the hydrogen atom possesses the flat, disc-like shape required by the Bohr model can be investigated experimentally as follows. Hydrogen atoms (from hydrogen canal rays) are shot into a crowd of gas molecules at rest. The H-atoms penetrate a certain distance into the gas, until they have given up all their excess energy. The extent of this penetration, considered as a problem of diffusion by the kinetic theory of gases, depends on the cross-section of the H-atoms (Vol. III, p. 307). Hence the considerations advanced above would lead us to predict that the extent of penetration would be diminished if the experiment were repeated with a magnetic field in the direction of the atomic beam. For on the theory that the magnetic moments of the atoms are due to the orbital circulation of their electrons, the atoms must set themselves with the plane of their electron orbits normal to the direction of the beam and so present the full area of their discs to the gas molecules in the collisions, i.e. must show a greater cross-section than they do in the absence of the field, when their orientations are random. The actual experimental performance of this test gives the result that the effective cross-section of the hydrogen atom is the same with the field as without.

Thus hydrogen atoms behave as if their cross-section were **unaffected** by the experimentally-proved quantized orientation of their magnetic moments in a magnetic field, i.e. as if they were **spherically symmetrical.**

A further difficulty is the fact that the Zeeman splitting for hydrogen in weak fields does not give the " normal " pattern of three components as shown in fig. 62, p. 204, but a more complicated pattern. Only when the field is made very strong does the pattern become transformed into the " normal " triplet.

So far we have only mentioned the difficulties connected with the hydrogen atom. The difficulties which present themselves in connexion with atoms of more complicated structure increase in seriousness as the spectra are studied in greater detail. Some alteration of the atomic model is therefore essential in order to make it consistent with the facts. It has been found impossible to obtain satisfactory results by modifying or extending Bohr's model; the only possible step is to set up a completely new one. The new theory, which is much more nearly related to classical ideas and therefore from the very start avoids the inflexibility of the Bohr model, was put forward by Schrödinger in 1926. The results deduced from the Bohr model can then be regarded as a first approximation. But the new so-called wave-mechanical model is relatively difficult to visualize in a pictorial manner; hence Bohr's mode of description, from which the essential features of atomic phenomena can be rapidly and readily made out, is still frequently used. Moreover, it is possible to go quite a long way with the Bohr model without coming into disagreement with facts, provided that certain modifications are adopted in the allocation of quantum numbers and corresponding corrections are applied to the conclusions arrived at. These modifications do not form a part of the Bohr theory itself, but follow necessarily from the wave-mechanical theory. Before we can go any further into the details of atomic structure, we must become acquainted with the new wave-mechanical model (see next chapter, p. 257).

Effect of Electric Fields (Stark Effect with Hydrogen Atoms).—In 1913 Stark found that the wave-length of the light emitted by atoms

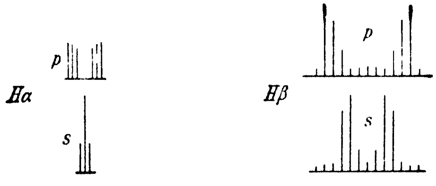

Fig. 68

Fig. 69

Figs. 68 and 69.—Stark effect, for the $H\alpha$ and $H\beta$ lines

is altered by the application of an electric field to the source. The originally simple lines of the spectrum are split up into numbers of sharp components. In the case of the hydrogen lines the following regularities are found. The number of components increases with the series number of the line. Thus, as we see from figs. 68 and 69, the Stark effect pattern is considerably more complicated for the $H\beta$ line than for the $H\alpha$ line. In the transverse effect (cf. fig. 62, p. 204) the electric vector of some of the components is parallel to the field (p-components), while that of the rest is normal to the field (s-components). In the longitudinal effect only the *s*-components appear, and they are unpolarized. Displacements and polarizations are symmetrical with regard to the undisplaced line. The distances of the components from the central line are integral multiples of a certain wave-number interval for all the hydrogen lines. Up to fields of about 100,000 volts per centimetre the displacements increase proportionally to the field strength.

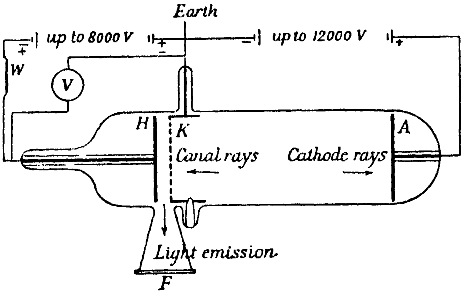

Fig. 70.—Arrangement for transverse observation

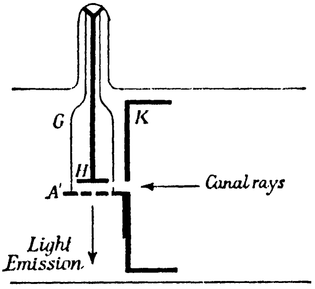

Fig. 71.—Arrangement for longitudinal observation

Figs. 70 and 71.—Stark's method for observing the Stark effect.

Either of two different principles may be used in the experimental observation of the effect.

Stark's Method.—In this method canal rays, produced in an ordinary gas discharge, are allowed to pass into a very strong electric field behind the perforated cathode. The experimental difficulty is to maintain this field without the occurrence of a discharge, in spite of the gas contained in the apparatus. Stark overcame this by placing the electrodes of the applied field very close together—a device which prevented any appreciable discharge (see Vol. III, p. 339). Figs. 70 and 71 show arrangements for transverse and longitudinal observation respectively.

Lo Surdo's Method.—In order to produce the Stark effect use may be made of the field in the cathode dark space which occurs in ordinary gas discharges just in front of the cathode. The strength of this field may be very great, but the method has the disadvantage that the exact magnitude and distribution of the field are not known. The observed Stark effect splitting may, however, be used to determine the strength and distribution of the field.

Fig. 72 shows an actual photograph obtained by Stark's method, the field being at right angles to the canal rays and the field electrodes being inclined to one another at an angle. The patterns of figs. 68 and 69 (p. 211) are plotted on a wave-number scale.

The Stark effect can be discussed in terms of the atomic model by considering the behaviour of an electron in the field of two positive charges. If one of the charges is then removed to infinity, we have the basis for the mathematical discussion of the case where a uniform electric field is superposed on the nuclear field. The details of the calculation cannot be given here. We must content ourselves with remarking that the presence of the external field distorts the electron orbits in a rather complicated way, since (at least in the case where one component lies in the orbital plane) the effect is to strengthen the nuclear field on one side of the ellipse and weaken it on the other. It is possible to determine a certain point (electrical centre) at which the potential energy of the electron at rest would be the same in the presence of the field as the mean potential energy during one revolution in the absence of the field. The distance of this point from the nucleus is found to be $3\varepsilon a/2$, where ε is the eccentricity and a the major semi-axis. Hence the atom must be regarded as an electric dipole with the moment $\mu_e = 3\varepsilon ae/2$. The electric centre describes an ellipse about the direction of the electric field with the frequency

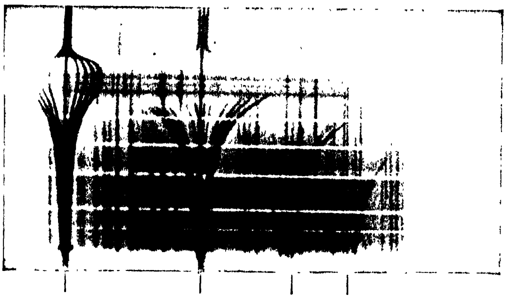

Fig. 72.—Splitting pattern for hydrogen in an electric field (Stark's method) up to 1·4 million volts per centimetre (small condenser, plate distance d = 0·1 to 0·3 mm.).

[From *Die Naturwissenschaften*, 1930 (Springer, Berlin).]

$$\nu_{\text{st.}} = \frac{3h\text{E}}{8\pi^2 mZe}\, n\, n_{\text{st.}}$$

where E is the field strength and the meanings of n and $n_{\text{st.}}$ are explained below. The energy of this motion is $h\nu_{\text{st.}}$.

The problem is a spatial one and hence involves three quantum numbers. These are designated by n_η, n_ξ, and n_ψ, corresponding to the co-ordinates (actually parabolic) introduced in the mathematical treatment. As in the cases previously mentioned, we have $n = n_\xi + n_\eta + n_\psi$. Instead of n_ψ it is usual (cf. p. 199) to introduce $r = n_\psi - 1$. Hence $n = n_\xi + n_\eta + r + 1$. Further, $n_{\text{st.}} = n_\eta - n_\xi$. The possible values are $0 \leqq n_\eta \leqq n - 1$; $0 \leqq n_\xi \leqq n - 1$. Considerations similar to those outlined on p. 205 show that $\Delta r = 0$ or ± 1, the first alternative leading to the p-components and the latter to the s-components.

From the formula given above it follows that the total energy in a given state is

$$-\text{W}_{\text{st.}} = -\text{W}_0 - \frac{3h^2\text{E}}{8\pi^2 mZe}\, n(n_\eta - n_\xi).$$

If the field strength E is measured in volts per centimetre, the energy difference $\text{W}_{\text{st.}} - \text{W}_0$ relative to the unperturbed state (expressed in wave-numbers) is found to be

$$\Delta\bar{\nu} = 6{\cdot}45 \,.\, 10^{-5}\left(\frac{\text{E}}{\text{Z}}\right) n(n_\eta - n_\xi)\ \text{cm.}^{-1}.$$

This method of deriving the energy value is only an approximate one. Actually the energy of the atom in the electric field may be expressed in the form of a series in ascending powers of E, namely, $\text{W} = \text{W}_0 + \text{AE} + \text{BE}^2 + \dots$. The argument given above takes only the linear term into account. The occurrence of the quadratic term is related to the fact that the field induces in the atom a proportional dipole moment, $\mu = \alpha\text{E}$ (cf. Vol. III, p. 101).

The value given above, moreover, holds only when the external field is sufficiently strong, i.e. when the energy change due to the field is large compared with that due to the variability of the mass of the electron. This condition is realized in practically all the experiments with hydrogen. If the field is relatively weak, the precessional motion of the orbit due to the variation in the mass of the electron is not suppressed and causes a displacement of the electrical centre. In the case of a sufficiently strong field, this electrical centre always lies on the same side of the plane through the nucleus normal to the field; consideration of fig. 57 (p. 201), however, shows that if the field is weak the electrical centre will lie on one side of this plane during one half of the rosette motion and on the other side during the other half of the motion. The sign of the energy is also reversed, since the field of the nucleus is thus weakened in the part of the orbit where it was previously strengthened. The linear term in the series for the energy is thus alternately positive and negative and its time-average is zero. Hence the first term which has to be taken into account is the very small quadratic term. The terms of higher order than the first also become appreciable at very high field-strengths (above 100,000 volts per centimetre — so-called quadratic Stark effect and Stark effect of higher order).

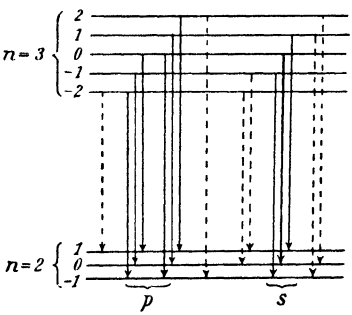

Fig. 73.—Splitting of the energy levels of the hydrogen atom in an electric field. The dotted transitions occur with very low intensity.

Fig. 73 shows the splitting of the energy levels of the hydrogen atom and also the transitions giving rise to the pattern for Hα shown in fig. 68 (p. 211). The intervals between the displaced levels are integral multiples of 6·45 × 10^5E cm.$^{-1}$. The Bohr model accounts excellently for the experimental data, and the numerical factor 6·45 is confirmed by the most recent measurements.

It may also happen that the external field becomes of the same order of magnitude as the nuclear field. On the portion of its orbit where the external field is opposed to the nuclear field the electron is then subject to practically no force and the orbit becomes indeterminate. Under these conditions there can be no energy transitions from or to the orbit. The necessary field-strength decreases as the principal quantum number increases, since the size of the orbit is proportional to n^2 and hence the force of attraction by the nucleus is inversely proportional to n^4. This suppression of certain transitions can be seen very well in fig. 72 (p. 213). The magnitude of the splitting of the Hβ line on the left shows that the field-strength increases from the bottom of the figure towards the top, passes through a maximum, and then falls off rapidly again. It will be seen that the lines disappear as the field-strength increases, the disappearance occurring at lower field-strengths for the lines of higher series number. Calculation shows further that the short-wave components of the Stark effect pattern of each line correspond to transitions starting from orbits with perihelia directed towards the positive electrode of the applied field, i.e. orbits for which the applied field opposes the nuclear attraction as the electron passes through its position of closest approach to the nucleus. The long-wave components, on the other hand, are due to transitions from orbits for which the greatest weakening of the nuclear attraction occurs in aphelion, i.e. when the electron is at its maximum distance from the nucleus. This provides an explanation of the experimental fact, also visible in fig. 72 (p. 213), that the long-wave components of the Stark effect pattern of any given line disappear at lower field-strengths than the corresponding short-wave components.

CHAPTER IV

Waves and Corpuscles

A. LIGHT AS A WAVE-MOTION

1. The Emission of Light

The recognition of the electromagnetic nature of light has led to a practically complete explanation of all the phenomena of its *propagation*. Optical problems have been treated in detail from this point of view in Vol. IV. On the other hand, the phenomena of the *emission* of light and of the *transformation* of light energy cannot be explained in terms of the electromagnetic wave theory. It has already been shown on p. 186 that the idea of an atom as an electrical transmitter of the kind considered in ordinary electrodynamics is incapable of accounting for the observed sharpness of spectral lines and the series relationships between them. The correspondence principle, however, indicates the existence of certain connexions with classical electrodynamics and furnishes a basis for the understanding of the intensities and states of polarization of spectral lines.

It has not yet been found possible to construct a bridge between those phenomena which can be explained by electrodynamics and those which can only be accounted for by the quantum theory. In particular, the process of the emission of light, i.e. the detailed mechanism of the passage of energy from matter to radiation, remains quite obscure. This undoubtedly constitutes one of the most important problems of modern physics.

The following is a summary of the phenomena associated with light emission, in so far as they are known and can be interpreted in terms of the undulatory theory.

Duration of Emission.—In the first place it may be assumed that the emission from atoms (at least in the gaseous state at relatively low pressures) is a perfectly random occurrence, i.e. that the trains of light waves sent out by any two atoms are *incoherent* (see Vol. IV, p. 3; cf. p. 218). Conversely, coherence may be taken as proof that the emission is from *one and the same* atom. By causing different parts of a wave-train to interfere it is possible to determine up to what path difference coherence is maintained, i.e. to find the length of the wave-train in question. In this way it has been found (GEHRKE and LAU, 1931) that interference effects are produced up to a path difference of 2·4 metres or 5×10^6 wave-lengths. Hence the coherent wave-trains must be at least as long as this. During emission these wave-trains detach themselves from the atom. Hence if we retain the idea that the emission takes place in the same way as in a macroscopic transmitter, we are led to the conclusion that the duration of the process giving rise to a single coherent train of waves is about 10^{-8} sec. It should be noted, however, that this duration is found even for the iron arc, in which the average time between collisions is only 10^{-10} sec. How it comes about that the emitted train of waves is coherent, in spite of the occurrence of about a hundred collisions during the act of emission, is still quite obscure.

W. WIEN used a different method to investigate the duration of the act of emission. He shot the emitting atoms into a vacuum in the form of canal rays and determined the length of path over which they remained luminous. The rays gradually become more diffuse and less intense as the distance increases. The point of excitation is known with fair accuracy, and thus if we assume that the atoms emit light immediately after excitation, the length of the luminous path and the measurable velocity of the atoms give the duration of the process of emission. The value obtained from the experiments is again about 10^{-8} sec. If we interpret the phenomena from the above point of view, the variation of the amplitude of the emitted wave-train during the emission process can be determined from the intensity of the luminosity at different distances from the point of excitation. This intensity falls off as the distance increases, and thus the observations seem to indicate that the coherent wave-trains are several metres in length and have a gradually decreasing amplitude. Since we know that the atom only has the quantity of energy $h\nu$ to emit (see for example the experiments of LENARD and HAUSSER quoted on p. 175), this must be the energy of each wave-train. In this way we arrive at the idea of a light quantum given in Vol. IV, p. 2. The *lateral extent* of each wave-train may be very great. Investigations of the diameters of stars by interferometric methods (see Vol. IV, p. 201) show that interference effects can be observed even when the mirrors are at a lateral distance of 30 metres apart, so that coherence still persists at this separation. Of course the angle subtended at the emitting atom is extremely small, and there is the possibility that different wave-trains may become merged together.

Statistical Interpretation.—The experiments with canal rays may, however, be interpreted in another way. As will be shown later (p. 233 *et seq.*), it is possible to regard the light quantum as a corpuscle which is shot out in a definite direction from the emitting atom. This view would suggest that the act of expulsion from the atom may occupy an interval of time which is very brief in comparison with 10^{-8} sec., though it is then impossible to explain the production of the long wave-train with its coherent properties. However, the falling off of the luminosity of canal rays may be interpreted in terms of individual acts of emission of very short duration—explosive expulsions of light quanta—provided that the occurrence of emission is assumed to be governed by a certain law of probability, as is the case for radioactive disintegration. According to this explanation of the phenomena, the time (10^{-8} sec.) deduced from the length of the luminous track of the rays is not the duration of the process of emission, but the average lifetime of the excited state, i.e. the average length of time during which an atom remains in the excited state before explosively expelling a light quantum.

Another interesting experiment is that in which canal rays emitting radiation are passed through an electric field and the emitted spectrum is observed in order to find out whether the wave-lengths sent out from the different points are those anticipated from the STARK effect for the respective local field-strengths. In particular, such an experiment can show whether, when the rays pass from a strong electric field into a region where there is no field, the normal emission is resumed in an interval of time which is brief in comparison with 10^{-8} sec. The results obtained (especially by RAUSCH VON TRAUBENBERG) indicate that the emission of light at any point is determined entirely by the field-strength at that point. Experiments on the coherence of light from points of different field-strength would be of great interest.

Very serious difficulties stand in the way of an explanation of these STARK effect phenomena in terms of emission processes of long duration; for according to p. 178 the sharp lines sent out in the electric field involve the emission of whole light quanta. The statistical theory, on the other hand, gives a satisfactory explanation of the observed facts.

2. Experiments on the Light emitted from an Atom

It would be possible to decide between the two modes of interpretation given above by observing whether rays from different parts of the same luminous canal-ray track are capable of giving interference effects. If interference between such rays were observable, this would mean that the rays were coherent and would form evidence in favour of the first mode of interpretation. Direct experiments of this kind have not yet been made owing to the practical difficulties.

RUPP, however, has carried out an experiment involving a similar idea. The light from the luminous canal-ray track was made to pass through a grating placed with its plane parallel to the direction of the canal rays and its lines normal to this direction. The grating consisted of alternate spaces and opaque bars of equal breadth a (about 0·5 mm.). On the view that the emission from each atom is a process occupying the whole time taken by the atom to traverse the luminous path length, the grating must let through a regular succession of equal fractions of the wave-train so emitted. If v is the velocity of the atoms in the canal rays, the length of each of these fractional wave-trains must be ac/v, where c is the velocity of light, and the path lag between corresponding points of successive fractions must be $2ac/v$. Each fractional wave-train was divided into two parts A and B by means of a half-silvered mirror, and the part B was given a path lag relative to A by means of a layer of air of thickness d. The value of d was chosen in such a way that the path lag of the part B relative to the part A for any given fractional wave-train was just equal to the lag of the part A of the next fractional wave-train. If the two fractions are coherent, interference must be observed under these conditions; and it was actually observed. This result would appear to furnish evidence in favour of the view that the process of emission of light from an atom is of relatively long duration; but it seems that an interpretation in terms of an "infinitely" rapid process of emission can also be put forward, so that the experiment cannot be regarded as conclusive.

A further question arises concerning the spatial form of the electromagnetic wave-train emitted from an atom. According to the classical theory, the wave-front must be spherical, the distribution of intensity in the particular case of a linear oscillator being that given in Vol. III, fig. 28, p. 627. From this it follows that rays emitted from an atom in exactly opposite directions must be capable of interference. Interference up to very large angles appears to have been actually demonstrated by the experiments of SELENYI (1911). He introduced a very thin layer of a fluorescent solution (the thickness being small compared with the wave-length involved) between plates of mica and glass and observed interference between the rays I and II (see fig. 1) which on emission must have made the large angle ϕ with one another.

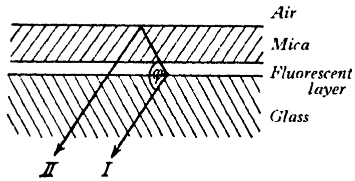

Fig. 1.—Interference of rays making a large angle with one another at emission

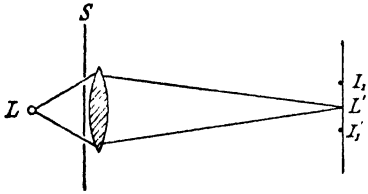

Fig. 2.—Schrödinger's interference experiment (I_1 and I_1' are interference maxima)

Experiments with incandescent wires have also been carried out by SCHRÖDINGER, using the apparatus shown diagrammatically in fig. 2. Actually WOLLASTON filaments * were used and interference effects were observed up to an angle of 57°. GERLACH and LANDÉ have also shown that the different fringes of the diffraction pattern of a slit are capable of interfering with one another.

* These are very thin platinum wires (diameter a few microns) covered with a layer of silver to make them more robust for manipulation. Once the filament has been mounted in a manner suited to the particular experiment, the silver layer is dissolved off with nitric acid, leaving the platinum core.

When extended sources of light are used, account must be taken of the superposition of the interference effects corresponding to the different points of the source. Sharp interference effects can only be obtained if the maximum distance between the points of the source, as viewed along the direction of the interfering rays, does not exceed a certain value depending on the wave-length and the angle between the rays used. The fact that the different points emit light of different relative phases has no effect upon the observed result, which depends only on the phase *differences* determined by the experimental arrangements.

The general conclusion from all the experiments on the interference of light hitherto is that a satisfactory explanation of the phenomena can be given in terms of the classical theory of electromagnetic wave-trains of wide aperture. This theory, however, involves difficulties whenever questions of the interchange of energy between radiation and matter are raised (see further p. 238).

3. The Form of Spectral Lines

Breadth of Emitted Lines.—The maximum path difference for which interference effects can be observed is appreciably less than we should expect from the duration of the emission process, as deduced by Wien (see above). The chief reason for this is that a spectral line is never strictly monochromatic, but extends over a wave-length region of finite breadth (fig. 3). The various causes of this broadening will now be considered.

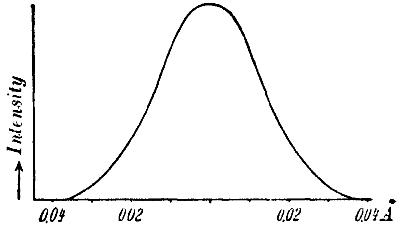

Fig. 3.—Form of the red cadmium line 6439 Å. (after P. P. Koch)

Doppler Effect.—The first cause is the thermal motion of the emitting atoms, which gives rise to a Doppler effect (Vol. II, p. 280). This effect, which consists in a change of observed frequency when the source has a velocity relative to the observer, is common to all wave-motions. The equation derived in Vol. II, p. 280 holds for light; that is,

$$\nu' = \nu\left(1 + \frac{v}{c}\right),$$

where v is the relative velocity of the source and c is the velocity of light. The sign of v is to be taken as positive when the source is approaching the observer and negative when it is receding from him.

Actually ν' has different values according as the source or the observer is moving relative to the medium (see Vol. II, p. 280); but the difference is only of the second order and is not observable at the velocities attained hitherto.

Experimental Measurement of the Optical Doppler Effect.—The DOPPLER frequency shifts are especially marked in the case of rapidly-moving heavenly bodies. Observation of the spectra thus gives a direct method of determining the velocity relative to the observer along the line of the ray (see fig. 4). In some cases the accuracy of determination may be within a few hundred metres per second. The effect can also be observed without difficulty in the laboratory, using canal rays. A Doppler effect also occurs by reflection at moving mirrors and is then twice as great for a given velocity, i.e. $\Delta\lambda = 2\lambda v/c$, where v is the relative velocity of the mirror with regard to observer. Similar alterations of frequency are caused by the thermal motions of the emitting atoms. Here the motions are distributed at random over all possible directions, so that the total result is a symmetrical broadening of each spectral line. The mean velocity of the atoms in the gaseous state is related to the temperature by the equation

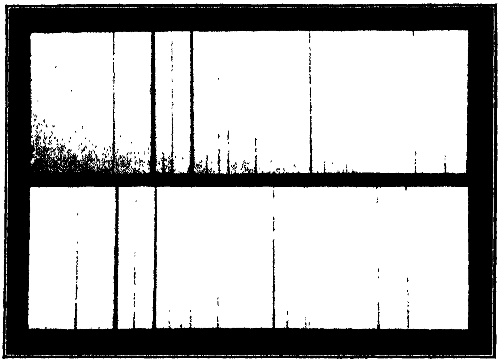

Fig 4.—Doppler effect in a stellar spectrum, showing a displacement of the sodium D lines corresponding to a relative radial velocity of 300 km. per sec.

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

$$\bar{v} = \sqrt{\frac{3kT}{m}}$$

(see Vol. II, p. 47), from which it follows that the broadening of spectral lines increases with rise of temperature and is greater for atoms of smaller mass. For example, the mean broadening $\Delta\nu$ for a hydrogen line at 0° C. (mean velocity 1·85 km./sec.) is $\pm 1{\cdot}85\nu/(3 \times 10^5) = \pm 6{\cdot}2 \times 10^{-6}\nu$. In the particular case of the Hβ line (for which $\bar{\nu} = 20564{\cdot}6$ cm.$^{-1}$) this gives $\Delta\bar{\nu} = \pm 0{\cdot}127$ cm.$^{-1}$.

Radiation Damping.—Even if the emitting atom is at rest, there is another cause of broadening of the spectral lines, namely, the fact that the wave-trains must be regarded as damped. According to the experiments of WIEN referred to on p. 216, the amplitude of the vibrations (to the square of which the intensity is proportional on the classical theory) falls off exponentially. Now we have seen in Vol. III, p. 630 that any oscillation of non-uniform amplitude can be regarded as made up of a number of components each of constant amplitude. Thus on account of the damping the otherwise monochromatic radiation is *modulated*, the degree of modulation increasing as the rate of damping increases.

This damping occurs with every electromagnetic oscillator which is not subjected to external forces, and can be calculated by the classical theory. The progressive decrease of amplitude is due to the fact that the emitter is losing energy by radiation. Hence this kind of damping is known as *radiation damping*. If, in accordance with experiment, we assume that the amplitude at time t is proportional to $e^{-\mu t}$, the time required for the amplitude to sink to half its original value is found, by a formula given by PLANCK, to be $5\lambda^2$ sec. approximately. This is in good agreement with experiment for visible light, for which (see p. 217) a value of about 10^{-8} sec. is observed. The corresponding half-value breadth of the $H\beta$ line (i.e. the distance from the middle of the line to the point at which the intensity is half that at the middle) is found to be $\Delta\lambda = 0{\cdot}83 \times 10^{-4}$ Å. This breadth, determined by radiation damping only, is called the *natural line breadth*. As we see from the numerical example, it is practically always negligible relative to the broadening due to the Doppler effect.

Collisional Damping.—Another kind of modulation of the emitted radiation is caused by the impacts of other atoms during the period of emission. These collisions interrupt the emission process, and a wave-train modulated by such interruptions may again be regarded as consisting of a large number of components of different wave-lengths. This so-called *collisional damping* effect is proportional to the number of impacts per unit of time, i.e. to the gas pressure. For a given gas pressure it is also proportional to the square root of the absolute temperature. Hence the effect becomes negligible at very low pressures and very low temperatures. Referred to 0° C. and 760 mm. pressure, the wave-number broadening due to collisional damping is of the order of a few cm.$^{-1}$, i.e. is quite considerable.

Stark Effect.—The observed breadths of spectral lines are generally somewhat greater than those calculated from collisional damping. The reason is that the electromagnetic fields of the colliding atoms disturb the emitting oscillator and change its frequency (Stark effect, see p. 211). This explains how in many cases the broadening depends on the nature of the atoms which collide with the emitter. The influence of similar atoms (called by LENARD the *Nähewirkung*—literally "proximity effect") is particularly great. The broadening of the mercury line 2537 Å. produced by mercury vapour at 7·3 mm. pressure is as great as that produced by the addition of an inert gas at 250 mm. pressure to highly rarefied mercury vapour. Thus, as we may expect from the very self-contained nature of their fields (see p. 334), atoms of the inert gases have a particularly small effect. The fields occurring in the electrical discharges during the excitation of the atoms may also cause considerable broadening of the spectral lines, especially in the neighbourhood of the electrodes. Fig. 5 shows examples of line broadening under different discharge conditions.

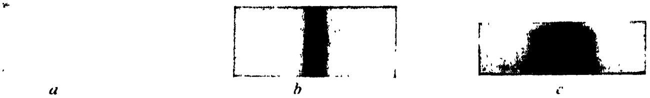

Fig. 5.—Broadening of the Hβ line arising from change of pressure and conditions of discharge. *a*, Feeble current at 1 mm. pressure. *b*, Spark (with condenser) at 1 mm. pressure. *c*, Spark (with condenser) at 760 mm. pressure.

[From *Handbuch der physikalischen Optik* (J. A. Barth, Leipzig).]

Self-Reversal.—Further, the form of a spectral line may be considerably affected when the line is such that it can be absorbed by the atoms which emit it (e.g. the D lines of sodium), and when there is a density or temperature gradient in the gas. Under such conditions the emission is very intense at the regions of higher temperature or density, the line being much broadened by the effects described above. As the radiation passes through the cooler or less dense regions of the gas it is re-absorbed, but the absorption line has a relatively small breadth, corresponding to the conditions in these regions. Hence only the middle portion of the broad emission line is absorbed, and the resultant intensity distribution is as shown in fig. 6 (so-called *self-reversal*).

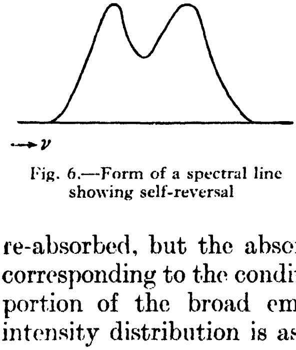

Fig. 6.—Form of a spectral line showing self-reversal

Hyperfine Structure.—Quite apart from the various kinds of broadening mentioned above, most spectral lines are in themselves not monochromatic, but consist of groups of several monochromatic components lying very close together. They are thus said to show a *fine structure* (as, e.g., the D line of sodium, which has two components with a separation of about 6 Å. or 20 cm.$^{-1}$) or a *hyperfine structure* (in which the separations of the components amount to only a few hundredths of a cm.$^{-1}$ (see p. 350)). The red cadmium line shown in fig. 3 (p. 219) is one of the few lines which appear to exhibit no marked complications. This is the reason why it was chosen for the evaluation of the metre in terms of wave-lengths of light (Vol. I, p. 7).

B. ENERGY AND MASS

4. Mass of the Energy of Light

On p. 647 of Vol. III it was shown that light exerts a pressure on the material bodies on which it falls. The magnitude of this radiation pressure on a reflecting surface is given by $p = 2S\cos^2\alpha$, where S is the energy-density and α the angle of incidence.

Hence, as was first pointed out in 1904 by **Hasenöhrl**,* it is possible to ascribe to light a certain momentum and consequently (by analogy with the momentum of material bodies) a certain mass.

According to this view, an enclosure containing electromagnetic radiation must have a mass proportional to the radiation energy enclosed in it. This can be deduced from observation by the following line of reasoning, which is due to **Lenard**. The enclosure, imagined as having parallel sides as in fig. 7, is assumed to have perfectly reflecting walls, so that any radiation which is once enclosed in it will be reflected to and fro continually without escaping. Let the enclosure be moving with an *acceleration* in the direction of the arrow marked v in the figure. In the first place consider only radiation which is propagated in the direction parallel to the direction of motion of the enclosure. This radiation will be reflected to and fro continually between the faces a and b. As a result of the Doppler effect the wave-length λ is changed at each reflection by the amount $\pm 2\lambda v/c$, where v is the velocity of the enclosure and c the velocity of light. A given amount of radiant energy is not altered by reflection, but the volume it occupies is increased or decreased in the same proportion as the wave-length. Since v/c is very small relative to unity, the energy-density, which is inversely proportional to this volume, must be changed by the fraction $\mp 2v/c$. If the mean energy-density in the enclosure is S, we may regard $\frac{1}{2}S$ as being propagated in the direction ab and $\frac{1}{2}S$ in the opposite direction ba. Hence the change of energy-density at each reflection is $\mp Sv/c$, the positive sign referring to the case in which c and v are in opposite senses. It follows that when the enclosure is moving with an acceleration there must be an energy-density gradient within it. For the radiation which has been reflected at the face b and is moving in the direction ba must have a greater density in the neighbourhood of b than in the neighbourhood of a,

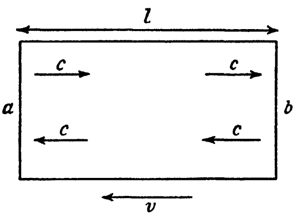

Fig. 7.—Pressure of radiation in an enclosure which is in accelerated motion.

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* **Fritz Hasenöhrl, born in 1874, became professor at the University of Vienna in 1907; he was killed in action in 1915.**

because the waves which are nearer a at a given moment must have been reflected earlier by the mirror b than those which are nearer b at the same moment, i.e. the waves which are nearer a must have been reflected when the velocity v of the mirror b was smaller than when the waves which are nearer b were reflected. Similarly, the radiation which has been reflected at the face a and is moving in the direction ab must also have a greater density in the neighbourhood of b than in the neighbourhood of a. The density difference δS must correspond to the change of velocity δv of the enclosure in the time $\delta t = l/c$ which the light takes to travel the distance l between the faces a and b, i.e. $\delta S = S\delta v/c$. But $\delta v/\delta t = f$, the acceleration of the enclosure. Hence we have $\delta S = Slf/c^2$. Now this difference of energy-density must be associated with an equal difference of radiation pressure on the two faces a and b, the smaller pressure being on the face a when the acceleration is directed in the sense ba. Multiplying this pressure difference by the area A of the faces in question, we obtain the force $P = SlfA/c^2$ which must be exerted in the direction ba in order to maintain the acceleration f. The fact that this force is necessary to maintain the acceleration is *due solely to the presence of the radiation* within the enclosure. Since the volume of the enclosure is lA, the quantity W of radiant energy contained in it is equal to SlA. Hence the force P is Wf/c^2. Division of this force by the acceleration (see Vol. I, p. 66) gives the mass m which is to be ascribed to the energy content W. We obtain

$$m = \frac{W}{c^2}.$$

To an amount W *of radiant energy must be ascribed a mass* W/c^2.

The corresponding momentum is

$$J = mc = \frac{W}{c}.$$

The energy W may be regarded as made up of light quanta each of energy $h\nu$, where ν is the frequency of the radiation. Then if m_L is the mass of each quantum, we have $m_L = h\nu/c^2$. The corresponding momentum J_L is given by $h\nu/c$ or h/λ.

If we assume that the law of reflection holds for a moving mirror when the angle of incidence is measured relative to the mirror, consideration of the radiation moving at right angles to ab likewise shows that there must be an energy-density gradient in the direction ab when the enclosure is moving with the acceleration f. If α is the very small angle of aberration v/c, the energy-density changes on reflection at a and b are found to be α times smaller than in the case considered above. On the other hand, the corresponding time δt is $1/\alpha$ times greater, so that the two factors cancel one another and the same result is obtained as before.

5. Mass of the Kinetic Energy of Electrons

Mass of Moving Electrons.—We have already seen on p. 322 of Vol. III that the mass of an electron is not constant but increases as the velocity increases.

In the first place we shall consider the experimental results. The principle of the experiments is to determine the specific charge e/m for electrons moving with different velocities, using the method of deflection by electrostatic and magnetic fields (see Vol. III, p. 314).

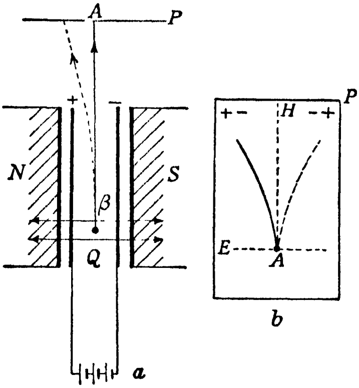

Fig. 8.—Deflection of electrons in parallel electrostatic and magnetic fields. (The plane of the figure on the right is at right angles to QA.)

Kaufmann used simultaneous deflection by an electrostatic field and a magnetic field, the two fields having the same direction (fig. 8*a*). In fig. 8*b* the point A represents the point of impact of a narrow beam of electrons moving directly away from the observer in the absence of any applied field. When the electrostatic field is applied, the electrons are attracted towards the positive plate. If we assume that the source of electrons gives electrons of widely differing velocity, the point A is thereby drawn out into the dotted line AE. The electrostatic deflection is proportional to $1/(mv^2)$. The action of the magnetic field alone is to deflect the electrons at right angles to the lines of force and thus to draw out the point A into the dotted line AH. The magnetic deflection is proportional to $1/(mv)$. When both fields are applied simultaneously, the parabolic curve of fig. 8*b* is what we should expect on the assumption that e/m is the same for all velocities. Reversal of the electric field will give the dotted parabola instead of the one shown as a continuous curve. Each point of the parabola corresponds to electrons of a certain velocity.

In actually carrying out this experiment Kaufmann used as electron beam the β-rays from Ra, which contain electrons of widely differing velocities up to values approaching the velocity of light. The trace he obtained upon the receiving plate was not that anticipated according to the considerations put forward in connexion with fig. 8. The actual traces obtained were as shown by continuous lines in fig. 9, the predicted parabolic curves being indicated by dotted lines.

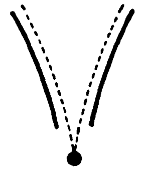

Fig. 9.—Diagram of observed deflection of electrons of very high velocity.

If we assume that e, the charge of an electron, is independent of its velocity, the observed result must be regarded as indicating that the mass increases with the velocity.

From these early experiments it was not possible to deduce the exact law of the change of mass with velocity. This necessitated the application of other methods, in which connexion we may mention the work of **Bestelmeyer** (1907) and more particularly the experiments of **Bucherer** (1909), which were refined by **Wolz** and **Neumann**, of **Hupka** (1910), and of **Guije**, **Ratnowski** and **Lavanchy** (1921).

The principle of **Bucherer**'s method is as follows. Electrons (β-rays) from a point source (radium preparation) pass through a condenser whose length is large compared with the distance between the plates (see fig. 10). At right angles to the field of the condenser there is a magnetic field of a strength exactly compensating for the electrostatic deflection of the electrons for one particular velocity v given by the equation $eE = -evH$, where E and H are the electrostatic and magnetic field-strengths respectively. It follows that only electrons of velocity $v = -E/H$ can emerge from the condenser; for all those with other velocities strike the condenser plates. When once the electrons have got clear of the condenser, they are subject to the action of the magnetic field alone and their paths therefore become arcs of circles (see fig. 10). The values of e/m for different velocities v can be calculated from the observed curvature for different electrostatic and magnetic field-strengths. The chief difficulty of the method is to allow correctly for the "edge effect" of the condenser field. The actual length of the condenser was 5 cm., and the distance between the plates only 0·25 mm. The distance of the receiving plate P from the condenser was 4–5 cm., the electrical potential difference about 100 volts, and the magnetic field about 100 gauss. The observed deviations are then of the order of magnitude of 1 cm.

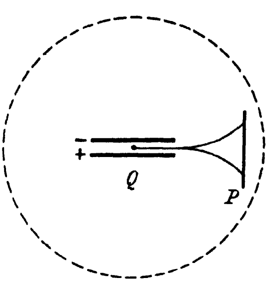

Fig. 10.—Bucherer's method for determining e/m at different velocities.

The method used by **Hupka** is similar in principle. Electrons of definite velocity are obtained by accelerating photo-electrons in a known field. The determination of e/m again follows from observed magnetic deflections.

The Swiss workers **Guije**, **Ratnowski**, and **Lavanchy** used crossed electric and magnetic fields and cathode rays produced in gas discharges. The same deflection is always produced, the potential difference of the condenser being varied for the different velocities. This method assumes that the value of e/m_0 is known.

The result of all these experiments is to show that the variation of the mass of an electron with its velocity v is best expressible by the equation

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}},$$

where c is the velocity of light and m_0 is the mass of the electron at very low velocities (the so-called *rest-mass*).

Fig. 11 shows how well this equation fits the experimental results. The points plotted are the values of e/m_0 calculated by means of the equation from the values of e/m observed by different workers for different velocities v. The important point is not so much the absolute value of m_0, but the fact that there is no variation of this value with velocity: it is the constancy of m_0 which proves that the equation is applicable over such a large velocity range.

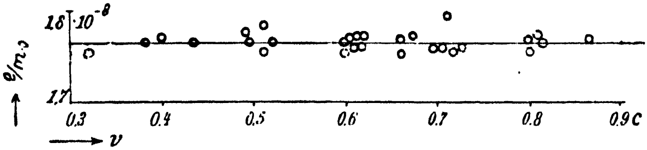

Fig. 11.—Values of e/m_0 calculated from observations on electrons of different velocities v by the formula $m_0 = m\sqrt{1-\left(\frac{v}{c}\right)^2}$

For the experiments of Rupp, which involve a quite different principle, see p. 254.

Mass ascribable to Kinetic Energy.—This relation* between the mass and velocity of the electron leads to the view that *kinetic energy also possesses mass and that the magnitude of this mass is given by* $m = E_{\text{kin.}}/c^2$, i.e. by an equation of the same form as for radiant energy. This result can be deduced by the following simple argument, which was first put forward by Lenard. A force F acts on a mass m so as to give it an acceleration f. The velocity at a given time being v, the distance ds covered in the element of time dt is given by $ds = v\,dt$ and consequently the work done by the force is given by $dE = F\,ds = Fv\,dt$. According to the view put forward above, this increase of energy corresponds to an increase of mass $dm = dE/c^2$. Now the fundamental law of mechanics may be written as

$$F = mf = m\,dv/dt$$

or $m\,dv = F\,dt$. As experiment has shown that the mass is not constant but depends on the velocity, it is necessary to make use of the formulation originally given by Newton (Vol. I, p. 78), namely

$$d(mv) = F\,dt.$$

From this we obtain

$$v\frac{dm}{dv}\frac{dv}{dt} + m\frac{dv}{dt} = F.$$

Substituting this value of F in the equation $dE = Fv\,dt = c^2 dm$, we obtain

$$v^2 dm + mv\,dv = c^2 dm.$$

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* On the theoretical side, the relation is one of the fundamental results of Einstein's theory of relativity.

As can be verified by differentiation, the solution of this differential equation is

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}},$$

where m_0 is the rest-mass. Thus when a mass m_0 is given a velocity v, the mass is increased by the factor $1/\sqrt{1 - v^2/c^2}$. This increase, which depends only on v^2, corresponds to the energy taken up in virtue of the acceleration, i.e. to the kinetic energy. Its value is independent of direction.

Magnetic Field of a Moving Charge.—The nature of the inertia of an electric charge can be investigated further by means of the FARADAY-MAXWELL theory. Reference has already been made on p. 439 of Vol. III to the analogy between the phenomena connected with self-induction on the one hand and the inertia of mass on the other. The fact that matter may be regarded as an assemblage of electromagnetic fields makes the view probable that the two sets of phenomena may be identical in their nature. According to this view, the inertia of mass is due to the increase in the strength of the magnetic field which is always associated with charges moving with an acceleration. As is stated by the equation $H = E_n v/(377\ c)$ given on p. 197 of Vol. III, the magnetic field-strength is proportional to the velocity, provided that the distribution of the lines of force remains unchanged. From this proportionality it follows that the inertia is always the same for a given acceleration and independent of the initial velocity from which the charge is accelerated. Experiment shows, however, that this is not true; the inertia (i.e. the mass) varies with the velocity. Since the above proportionality of magnetic field strength to velocity is not open to doubt provided the field distribution remains the same, we are forced to the conclusion that the field distribution must vary with the velocity. Such a variation is indeed to be expected from the longitudinal tension and lateral repulsion of the lines of force.

We now proceed to consider this more closely. The tension and lateral repulsion of the lines of force are equal to one another at every point, both for the electric field (Vol. III, p. 98) and for the magnetic field (Vol. III, p. 430), being in both cases equal to the energy-density at the point considered. If an electric field moves with the velocity of light in a direction at right angles to the lines of force, the energy-density of the magnetic field becomes equal to that of the electric field at every point (Vol. III, pp. 197 and 617). In this case the tension and lateral repulsion of the lines of force of both fields are equal. If the electrical energy-density in a certain region of the field is $S_e = \frac{1}{2}K_0E^2$, the magnetic energy-density for a velocity v of motion at right angles to the electrical lines of force is $S_m = \frac{1}{2}\mu_0H^2 = \frac{1}{2}\mu_0E^2v^2/(377\ c)^2$. From this by a simple calculation we obtain $S_m = \frac{1}{2}K_0E^2v^2/c^2$. Now the magnetic lines of force are at right angles to the electric lines of force. Therefore the tension along the latter is reduced by the lateral repulsion between the former, so that the resultant tension along the electric lines of force is $T = \frac{1}{2}K_0E^2[1 - (v^2/c^2)]$. It follows that T vanishes when $v = c$. The lateral pressure in the plane normal to the direction of motion is reduced to the value $L_\perp = \frac{1}{2}K_0E^2[1 - (v^2/c^2)]$; that in planes parallel to the direction of motion is increased to $L_\parallel = \frac{1}{2}K_0E^2[1 + (v^2/c^2)]$.

Hence if a plate condenser is moving in the plane of the plates, i.e. at right angles to the electric lines of force, the attraction between the plates decreases as the velocity increases. Two opposite charges moving with the velocity of light in a direction normal to the line joining them do not attract one another. This is the reason why the electromagnetic fields of light, which are propagated with the velocity *c*, do not collapse, i.e. do not shrink up like the lines of force about a conductor when the current flowing in it is stopped. This shrinking together only occurs when the velocity *c* is destroyed. Then the whole of the energy of the light is given up. Thus light possesses no rest-mass (see below).

Application of these ideas to a region of space which is spherical when at rest and contains charges, i.e. whose field distribution possesses spherical symmetry (fig. 12*a*), gives the following result. When the region is in motion, the magnetic field-strength and hence also the diminution of the lateral pressure of the electric lines of force are greatest in the equatorial plane (i.e. the plane at right angles to the direction of motion), because the lines of force are all at right angles to the direction of motion. The electric field component in the direction of motion, on the other hand, is not associated with a magnetic field. Hence the greater lateral pressures outside the equatorial plane drive the electric lines of force into this plane until the lateral pressure of the intensified electric field there once more establishes equilibrium. Thus the polar regions become poorer in electric lines of force (fig. 12*b*), in the same proportion as the magnetic lines of force in the equatorial direction weaken the lateral pressure between the lines of force of the field. When *v* becomes equal to *c*, all the lines of force emanating from the charges are driven into the equatorial plane.

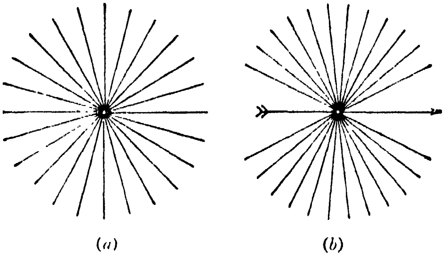
(*a*) (*b*)

Fig. 12.—Distribution of the lines of force of an electron (*a*) at rest and (*b*) in motion

Since the component E_n of the electric field-strength normal to the direction of motion increases with the velocity, the magnetic energy associated with the moving charges must increase *more rapidly* than if the field distribution remained unaltered. Hence the inertial resistance for a given increase in velocity must be greater for greater initial velocities, i.e. the mass must increase with the velocity. The law of this increase in mass depends on the field distribution. This in turn depends on the arrangement of the charges. Since, however, in the spherical region considered above the forces between the charges are altered by their motion, the arrangement of the charges must also be altered. When this is duly taken into account (H. A. Lorentz), a mass variability is deduced which agrees with observation.

Hence it follows that inertial energy (i.e. kinetic energy) is electromagnetic in character, being that portion of the total electromagnetic energy of the given system which depends on the state of motion of the system and which must be taken away from the system in order to bring it to rest.

6. Mass as Energy

Generalization.—The relationships between mass and energy discussed in the preceding sections lead to the view that *every* mass may be regarded as energy and that energy is the fundamental concept on which the concept of mass depends. According to this view, *all* energy changes must be associated with corresponding changes of mass, given by the equation $W = mc^2$.

Experiment shows that mass is in general conserved in physical processes. Hence it follows from the above generalization that energy must also be conserved.

Mass as Energy.—We may express the above generalization as follows:

Every mass m *is equivalent to an energy* $W = mc^2$. *i.e. under suitable conditions it may be transformed into this energy. Conversely, every amount of energy* W *is equivalent to the mass* $m = W/c^2$.

The energy of a mass m_0 (rest-mass) moving with the velocity v is accordingly given by the general formula

$$W = \frac{m_0c^2}{\sqrt{(1 - v^2/c^2)}} = m_0c^2 + \tfrac{1}{2}m_0v^2 + \tfrac{3}{8}m_0\frac{v^4}{c^2} + \ldots$$

Velocity of Light as the Limiting Velocity.—From the foregoing equations, whose general validity is being steadily confirmed by increasing experimental knowledge (see below), it follows that an infinitely great energy would be necessary in order to give a mass a velocity equal to that of light. Thus, so far as material bodies are concerned, the velocity of light is seen to be a *limiting velocity* which can only be approached asymptotically and never exceeded.

Difference between the Energy of Radiation and the Energy of an Electron.—The mass of a light quantum is not subject to the above relationships; for the quantum is shot out from the emitting system with the velocity of light, but its mass is only $m_L = h\nu/c^2$. A light quantum, moreover, possesses no rest-mass (see above). The difference is probably connected with the fact that an electron (or, in general, matter) is a system in which the lines of force actually end upon charges, whereas the light quantum involves only closed lines of force without ends. Hence the relation between the mass of the light quantum and its velocity is quite different from the corresponding relation for matter. This can also be seen from the following argument.

The boundary surface of a transparent medium irradiated by light is subject to a differential radiation pressure corresponding to the energy-density difference $(W/c_1) - (W/c)$, where c is the velocity of light in a vacuum and c_1 is the velocity in the medium, c_1 being less than c. This is associated with a change of momentum $M_1c_1 - Mc$ of the quantum, where M_1 is its mass in the medium. Since the frequency remains unchanged, the mass M_1 at the velocity c_1 is given by $M_1 = W/c_1^2$. Hence the mass is *greater* for smaller velocities of propagation, the excess being obviously derived from the medium through which the light passes.

Applications of the Energy-mass Relationship.—The consequences of this relationship may be expected to be chiefly evident in processes involving the transformation of very large quantities of energy, i.e. especially in nuclear transformations. Thus the accepted modern explanation of the deviation of the atomic weights of isotopes from whole numbers is that these deviations are due to the energy liberated in the building up of the nuclei. Again, in the case of atomic transmutations it is usual to introduce the mass change into the equation of transmutation as an energy change additional to the other energy changes (kinetic energy, radiation, &c.).

As an example we may calculate the energy which holds together the four elementary massive constituents (protons or neutrons) in the α-particle. For the sake of simplicity we may assume that the α-particle consists of four protons and two electrons. The mass of a proton is $1{\cdot}6609 \times 10^{-24}$ gm., that of an electron $9{\cdot}035 \times 10^{-28}$ gm. Four protons and two electrons would therefore have mass $4 \times 1{\cdot}6609 \times 10^{-24} + 2 \times 9{\cdot}0 \times 10^{-28} = 6{\cdot}645 \times 10^{-24}$ gm. Actually the mass of an α-particle is only $6{\cdot}598 \times 10^{-24}$ gm. The mass difference of $0{\cdot}047 \times 10^{-24}$ gm. must therefore be expended as energy in order to split up the α-particle into 4 protons and 2 electrons. The corresponding energy is found to be $4{\cdot}23 \times 10^{-5}$ erg per α-particle. For 1 gm.-atom this gives $4{\cdot}23 \times 10^{-5} \times 6{\cdot}06 \times 10^{23} = 2{\cdot}56 \times 10^{19}$ ergs $= 6{\cdot}13 \times 10^{8}$ kcal., which is some five million times greater than the energy set free by the combustion of 4 gm. of hydrogen. This calculation accounts for the great stability of the α-particle. So far as we know at present, the order of magnitude of the calculated energy is not affected if the α-particle is assumed to consist of two protons and two neutrons. Similar considerations also account for the stability of other nuclei. Thus the splitting up of a gramme-atom of oxygen O^{16} into its elementary constituents would require an energy expenditure of $2{\cdot}6 \times 10^{9}$ kcal. per mol.

Energy and Gravitation.—If it is true that every mass, including material masses, is due to energy, then we may expect that energy which is not associated with matter will be affected by gravity in the same way as material bodies are. A number of direct experiments relating to this question have been carried out. In one class of experiments attempts have been made to measure the possible difference between the inertial and the gravitational mass of energy (SOUTHERNS, 1910; ZEEMAN, 1918). The equality of inertial and gravitational mass can be demonstrated with great accuracy by the method of EÖTVÖS (see Vol. I, p. 194). For the present problem substances may be used which are known to possess a large amount of energy which they can give up in some process. It is natural to choose radioactive substances.

Thus the mass difference between 1 gm. of uranium and its end-products helium and lead, corresponding to the energy given out in the radioactive transformations, is of the order of magnitude of 10^{-4} gm. By comparing lead oxide and quartz with uranium compounds by the method referred to above, ZEEMAN was able to prove that the difference between gravitational and inertial mass cannot exceed one part in five millions. Thus these experiments demonstrate a proportionality between weight and mass for the energy which is contained in radioactive atoms and may be liberated by their disintegration. From this we conclude that *the energy stored up in the electromagnetic fields of atoms possesses a weight corresponding to its mass.*

A second class of experiments is concerned with the behaviour of radiation in a gravitational field. The action of a gravitational force at right angles to the direction of propagation was considered by J. SOLDNER (1804) on the assumption that light behaves as a mass travelling with the velocity of light. The effect is too small to be observed under terrestrial conditions, and so (as was pointed out by SOLDNER) it is necessary to investigate the deflection of light rays which, coming from stars, pass very close to the sun's edge. This can be done during total solar eclipses. If the light is attracted by the sun's gravitational field and " falls " towards the sun's centre, the deflection will cause an apparent increase of the angular distance between the star and the sun, as viewed by a terrestrial observer. The displacement will decrease with increasing distance from the sun's edge. For a material particle moving in a hyperbolic orbit with the velocity of light the magnitude of the displacement would be 0·87″ at the sun's edge. For electromagnetic radiant energy a value of the same order of magnitude is to be expected. The exact value will not be the same, because light has no rest-mass and hence (according to LENARD) there can be no gravitational effect on light in the direction of propagation, in which the velocity is always c. The actual experimental results still seem somewhat uncertain. The investigations are extremely difficult and there are many sources of error; in particular, it is not possible to allow accurately for the effect of the matter surrounding the sun. The most recent and, as it seems, the most reliable measurements (FREUNDLICH) give an extrapolated value of 2·3″ for the deflection at the sun's edge, while earlier American determinations had given the value 1·72″. The experiments so far carried out prove beyond doubt that *radiant energy is subject to gravitational forces in the transverse direction,* though as yet the exact law of the effect cannot be deduced from the observations.

At the present time nothing can be said with certainty about the effect of gravity on radiation in the direction of propagation of the latter. It is possible, for example, that light emitted from a star of great mass may have some of its energy transformed into potential energy, its velocity of propagation being thereby diminished like the velocity of a stone thrown upwards. According to electrodynamical laws, however, this is very unlikely. Alternatively, the velocity might remain constant, the diminution of energy resulting in a decrease of amplitude (and hence of intensity) or in a diminution of the frequency in accordance with the equation $\nu = E/h$. This latter effect would be observable as a displacement of spectral lines towards the red. Such displacement is found in the light from many distant spiral nebulæ, and is interpreted as a Doppler effect, due to speeds of recession proportional to distance. Since the rest-mass of light is zero, it is probable (according to LENARD) that the potential energy of light is always zero also. The passage of light away from a star is thus unattended by any increase of potential energy: not only does the total energy of the light remain constant (as is also true for a stone which is thrown upwards), but so does its velocity. According to this view, neither decrease of intensity nor spectral displacement towards the red (apart from possible Doppler effect) is to be anticipated.

C. THE CORPUSCULAR PROPERTIES OF LIGHT

7. The Photon

As we have seen above, light quanta may be regarded as packets of energy possessing mass and momentum. Thus they behave in a certain sense as if they were corpuscular in nature. Indeed, a large number of the properties of light can be accounted for by the theory that the quanta are particles of mass $h\nu/c^2$ (see Table XIX). In order to emphasize this corpuscular nature, the light quanta are often referred to as *photons*.*

TABLE XIX.—MASSES OF SOME LIGHT QUANTA

λ	ν sec.$^{-1}$	$h\nu$ ergs	m_L gr.	$m_L/m_{elec.}$
1 μ	3×10^{14}	$1{\cdot}96 \times 10^{-12}$	$2{\cdot}2 \times 10^{-33}$	$2{\cdot}42 \times 10^{-6}$
1 Å.	3×10^{18}	$1{\cdot}96 \times 10^{-8}$	$2{\cdot}2 \times 10^{-29}$	$2{\cdot}42 \times 10^{-2}$
1 X	3×10^{21}	$1{\cdot}96 \times 10^{-5}$	$2{\cdot}2 \times 10^{-26}$	24·2
24·2 X	$1{\cdot}24 \times 10^{20}$	$8{\cdot}1 \times 10^{-7}$	$9{\cdot}0 \times 10^{-28}$	1

If this view is correct, the incidence of light quanta upon electrons or atoms or other light quanta must give rise to effects similar to those observed in the collision of material particles. Several effects of this kind are actually known. One of the most important of these will now be considered.

The Compton Effect.—In 1922 A. H. COMPTON succeeded in showing that X-rays (especially those of short wave-length, e.g. Mo K-radiation, for which $\lambda = 0{\cdot}7$ Å.) scattered by light elements contain, in addition to the incident wave-lengths, other wave-lengths which are somewhat longer. This discovery was made possible by advances in X-ray technique. For the photographic exposures it was necessary to keep the loading of the tube constant at about 30 milliamperes and 50,000 volts over periods of two to three hundred hours.

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* Gr. *phōs*, light.

The experimental results show that X-rays suffer a change of wave-length on scattering, the magnitude of the change and the ratio of the intensities of the modified and unmodified rays being determined (other conditions being the same) by the angle of observation relative to the primary beam.

Fig. 13 is a diagram of the experimental arrangement. The X-rays emitted from the tube R are incident on the scattering substance S (e.g. graphite). A narrow scattered beam making the angle θ with the direction of incidence of the primary beam is selected by a series of slits in lead screens B. It is then spectrally analysed by means of a rotating crystal K, the actual observations being made either photographically or by means of an ionization chamber J (see figure) mounted on a divided circular scale. Fig. 14 shows photographic records and fig. 15 electrometer curves for different values of the angle θ. In addition to the lines of unchanged wave-length, the scattered spectra are seen to contain new and somewhat diffuse lines of longer wave-length. For each primary line there is one displaced line, the difference between their wave-lengths increasing with the angle of observation θ.

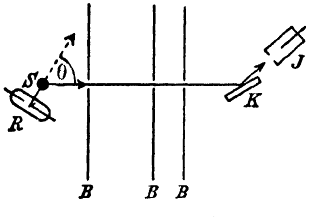

Fig. 13.—Experimental apparatus for measuring the wave-length change in the Compton effect.

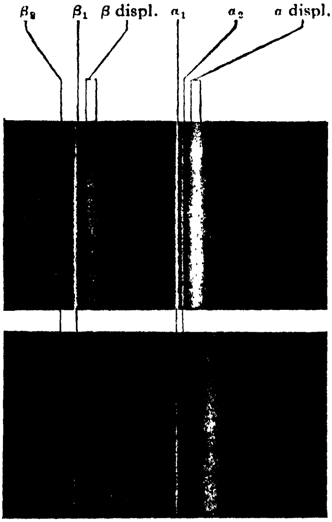

Fig. 14.—Photographic record showing the Compton effect. Above: angle of scattering 63½°. Below angle of scattering 90°.

[From *Handbuch der Physik*, Vol. XXIII (Springer, Berlin).]

It is a remarkable fact that the difference of wave-length $\Delta\lambda$ between corresponding unmodified and modified lines when $\theta = 90°$ is independent of the wave-length of the primary X-rays and of the nature of the scattering substance. The value of $\Delta\lambda$ is always $0{\cdot}024$ Å. On the other hand, the relative intensities of the unmodified and modified lines vary markedly with these factors. As the atomic number of the scattering atoms increases the intensity of the modified line falls off rapidly. The same is true for increase of primary wave-length. In the case of γ-rays, which are of very short wave-length, the scattered spectrum consists almost entirely of modified radiation. In the case of light, which is of relatively very long wave-length, only the unmodified lines can be detected (see also p. 380). Other conditions being the same, the relative intensity of the modified line also increases with the angle of observation θ (see e.g. fig. 15).

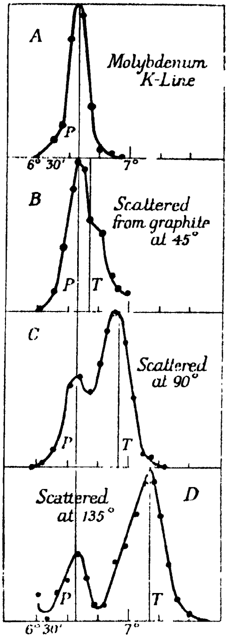

Fig. 15.—Electrometric record showing the Compton effect.

[From *Handbuch der Physik*, Vol. XXIII (Springer, Berlin).]

Theory of the Compton Effect.—The observed characteristics of the effect, especially the dependence of $\Delta\lambda$ upon the angle of scattering θ and its independence of the nature of the primary wave-length and of the nature of the scattering material, lead to the following interpretation.

The scattering of X-rays with change of wave-length may be regarded as due to the collision of a light quantum (photon) with an electron, both being assumed to be elastic spheres and the kinetic energy of the photon being taken as equal to $h\nu$. Such a collision is represented diagrammatically in fig. 16, wavy lines being used for the path of the photon and a straight line for that of the electron. Let ν_0 be the frequency of the primary X-rays and ν that of the rays modified by scattering. Further, let v be the velocity, m the mass, and m_0 the rest-mass of the electron. Let θ be the angle of observation (i.e. the angle between

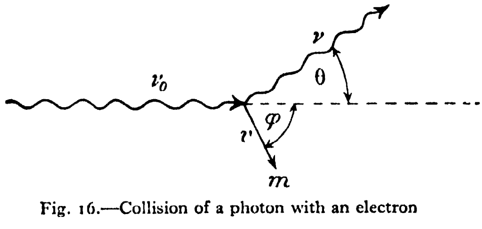

Fig. 16.—Collision of a photon with an electron

the direction of the scattered X-rays and that of the incident X-rays) and ϕ the angle between the primary direction and the direction in which the electron is struck. Taking account of the variation of the mass of the electron with its velocity, by the principle of conservation of energy we have

$$h\nu_0 + m_0c^2 = h\nu + \frac{m_0c^2}{\sqrt{1 - \beta^2}},$$

where $\beta = v/c$. The principle of the conservation of momentum gives for the direction of the primary beam

$$\frac{h\nu_0}{c} = \frac{h\nu}{c}\cos\theta + \frac{m_0v}{\sqrt{1 - \beta^2}}\cos\phi,$$

and for the direction normal to the primary beam

$$0 = -\frac{h\nu}{c}\sin\theta + \frac{m_0v}{\sqrt{1 - \beta^2}}\sin\phi.$$

The angle ϕ may be eliminated by squaring and adding these last two equations, after taking the terms in ϕ to one side. Then v may be eliminated by using the energy equation. This leads to the result

$$\nu = \frac{\nu_0}{1 + A(1 - \cos\theta)},$$

where

$$A = \frac{h\nu_0}{m_0c^2}.$$

From this we at once obtain the wave-length displacement, namely

$$\Delta\lambda = \frac{c}{\nu} - \frac{c}{\nu_0} = \frac{h}{m_0c}(1 - \cos\theta).$$

The numerical value of $h/(m_0c)$ is $0{\cdot}0242 \times 10^{-8}$ cm., so that when $\theta = 90°$ (i.e. $\cos\theta = 0$) the theoretical value of $\Delta\lambda$ is 0·242 Å., in agreement with observation (see above).

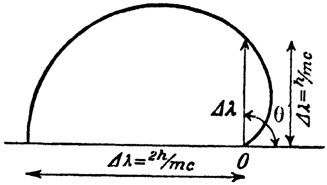

Fig. 17.—Variation of the wave-length change in the Compton effect with the angle of scattering.

In virtue of the principle of the conservation of momentum, the process must take place in a plane.

We see that this theory accounts for the fact that the wave-length change on scattering is independent of the scattering material and of the primary wave-length. The theoretical variation of $\Delta\lambda$ with the angle of scattering θ (represented in polar co-ordinates in fig. 17) is in excellent agreement with observation. In the region of very short wave-lengths (γ-rays) the wave-length change may be 100 per cent or more. In this region the frequency of scattering is also much greater, i.e. the relative intensity of the modified line is greater.

Further Experimental Results on the Collisions occurring in the Compton Effect.—If the above theory is correct, it ought to be possible to detect the recoil electron which is struck by the photon. In fact we have already met with it as a scattered electron in fig. 37, p. 55. The preferential distribution in the direction of the incident radiation is also apparent. In contrast to the photo-electrons, the recoil electrons only take up a fraction of the energy of the incident photon; hence their velocities are smaller than those of the photo-electrons and their path lengths (cloud-tracks) much shorter.

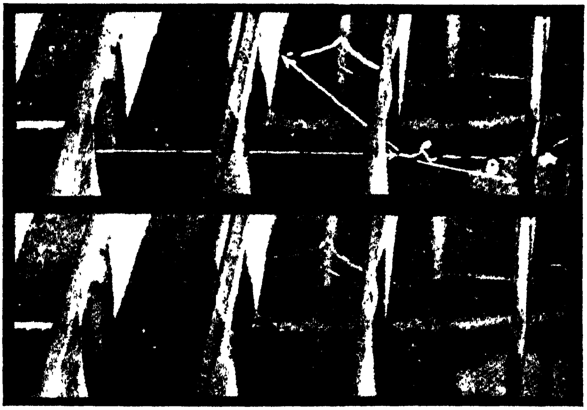

Fig. 18.—Cloud-chamber photograph showing the collision of a photon with an electron (after Compton)

[From *Zeitschrift fur technische Physik* (J. A. Barth, Leipzig, 1927).]

Fig. 18 shows a cloud-chamber photograph in which it is possible to make out both the track of the recoil electron and also that of the scattered quantum—the latter by means of a photo-electron liberated after the Compton-effect collision. Photographs of this sort make a direct test of the formulæ deduced above possible. Of a total number of 850 exposures, 38 showed both electron and scattered photon and 18 gave a relation between the angles in agreement with the theory given above. The relatively high proportion of exposures showing both electron and scattered photon furnishes proof that the scattering of the X-ray photon and the ejection of the electron from the atom concerned must be almost simultaneous processes. This question whether the two processes are simultaneous is answered even more conclusively by the experiments of Bothe and Geiger. These investigators set up two ionization counters very close together in a space filled with hydrogen (see fig. 19). One of these counters (shown on the right in the figure) was so arranged as to respond in the main to electrons; while the other, being

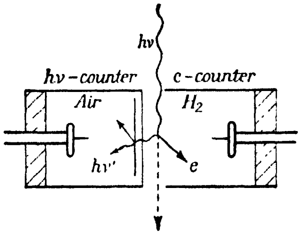

Fig. 19.—Diagram of the experimental apparatus for investigating the simultaneity of photon scattering and electron recoil in the Compton effect.

filled with air and closed with a platinum foil which absorbed electrons but transmitted X-rays, was sensitive only to X-rays. A primary X-ray beam was made to pass between the two counters and was scattered in the gas as indicated in the figure. It is clear that if the processes of scattering and electron ejection are simultaneous, then there must be a large number of simultaneous responses (" coincidences ") in the two counters. The actual experiment showed that the number of such coincidences was considerably greater than that to be expected from mere chance.

In the discussion given above it was assumed that the photon collides with a " free " electron, i.e. no account was taken of the forces binding the electron to its atom. The agreement between theory and experiment provides justification for this assumption, so far as the lighter elements are concerned. The effect of the forces binding the electron to its atom is probably to be seen in the broadening of the displaced lines. The absence of the effect in the case of visible light may be accounted for as due in part to the very small energy of the quanta in this region, but may be regarded as a consequence of the progressive approximation to classical electrodynamical behaviour with increase of wave-length.

8. Relation between the Corpuscular and the Undulatory Properties of Light

Up to the present it has not been found possible to overcome the difficulties which lie in the way of any attempt to reconcile the undulatory and corpuscular theories of light. In order to appreciate the magnitude of these difficulties, it is only necessary to recall that on the one hand experiment indicates existence of coherent wave surfaces of 30 metres width, while on the other hand the whole energy of a light quantum may be concentrated upon an atom and even (as may be seen in fig. 18, p. 237) upon the extremely small spatial region—of diameter something like 10^{-12} cm.—occupied by an electron. Moreover, numerous experiments have been carried out on the photoelectric effect at very low light intensities, and no departure from regularity has been observed. The number of photo-electrons liberated remains proportional to the incident intensity even when only a few photons are emitted from the source per second. Similarly, interference experiments at these very low light intensities give the normal distribution of interference fringes. Since interference phenomena undoubtedly indicate that the coherent properties of light have a certain extension in space (cf. SCHRÖDINGER'S experiment, p. 218), we are forced to make either the very improbable assumption that the atoms involved in the photoelectric effect are capable of suddenly collecting the necessary energy $h\nu$ out of a large spatial region, or else the equally improbable assumption that they gradually take up energy from the radiation field until the quantity $h\nu$ is accumulated and an electron is ejected. In the latter case, if the irradiation were terminated before the full quantity of energy $h\nu$ had been amassed by an atom, we should expect that the fraction would be given up in some way or other. **Joffé** and **Dobrowavoff** were able to show that a small particle of bismuth (diameter about 10^{-5} cm.) suspended in an **Ehrenhaft** condenser showed the photoelectric effect even when irradiated by X-rays of such low intensity that the alterations of charge occurred at intervals of half an hour.

Experiments have also been carried out with a view to subdividing the light quanta and then investigating the photoelectric effect produced by the parts. When a beam of light is separated into two partial beams by a semi-reflecting layer, it is found that both of the partial beams give the normal photoelectric effect; the intensity is proportionally less than for the original beam, but the velocity of the photoelectrons still corresponds to the full energy quantum $h\nu$. At the same time it must be borne in mind that the two partial beams are capable of showing interference effects, so that they must have originated in the same elementary process of emission.

It has further been found possible by means of Kerr cells to subject beams of light to periodic interruptions with a frequency of 10^9 per second (**Rupp**). Although the light quanta must thereby have been broken up into smaller parts, no alteration of frequency is observed such as might have been expected from the equation $\nu = E/h$ and the smaller energy of these parts. The only effect is a broadening or splitting of the originally monochromatic spectral line in accordance with the superimposed periodic modulation.

Thus while some of the observed phenomena indicate a continuous radiation field as required by classical electrodynamics, other phenomena point to a very intense concentration of the energy in small packets or photons. In certain cases, moreover, one set of experiments gives the one type of result and another set simultaneously gives the other type. This leads to the conclusion that the formulæ of classical electrodynamics, at least in the optical and short-wave regions, can only have a statistical meaning, i.e. they can only express the probability that a photon will be encountered at a given position in space. According to this view, a dark interference fringe is not to be regarded as due to the superposition of two spatially-extended wave-trains, but rather as a region which the special experimental arrangement prevents any photons reaching. From this point of view it is possible to explain the results of photoelectric experiments with very low light intensities, there being a certain probability that an atom will be struck by a photon whose energy is concentrated within a very small space. Thus the electrodynamically-determined field is to be regarded merely as a kind of *directing* field and the electric and magnetic vectors as having only a statistical significance. The intensity, as calculated on the wave-theory, then expresses the probability of an encounter with a photon at the position in question, i.e. the average rate of arrival of photons, as experimentally observed.

The present state of the problem is most unsatisfactory, and in spite of the recent advances in the theory of light emission (see p. 272 *et seq.*) no path leading to a solution can as yet be discerned. This state of affairs is strongly reminiscent of the initial stages in the development of the quantum theory (see p. 196), when the energy relationships involved in the interaction of matter and radiation were in accordance with the quantum postulates but their probability (i.e. the intensity and polarization of spectral lines) was deduced by reference to the classical wave-theory (correspondence principle). The development of a quantum electrodynamics is still at its beginning.

From the corpuscular properties of photons it must be concluded that they are shot out from the emitting atom within narrowly-defined solid angles (about 10^{-5} as deduced from the experiments of JOFFÉ referred to above) and that light quanta are not emitted in the form of spherical waves in accordance with classical electrodynamics (see Vol. III, fig. 27, p. 626). The term "light darts"* is sometimes used to emphasize the directional nature of light emission.

The question can be investigated further by the following experimental method. Imagine a radioactive preparation which emits γ-rays. Let the source be so weak that the irregularities arising from the time-variations in the radioactive disintegration are easily observable. If the γ-ray emission is in the form of spherical waves, there should be no differences in the intensity of the rays at different points around the source at a given distance from it. Thus suitable ionization chambers or counters placed at these points should register only the time-variations and should show no mutual variations dependent upon their positions. Experiments of this kind, carried out by E. MEYER in 1910, gave the result that γ-rays exhibit the same sort of directional variations as do the corpuscular α-rays. This makes it clear that the energy of γ-rays must be concentrated in just as small packets as the energy of α-particles, i.e. that γ-rays must be corpuscular as far as energy effects are concerned. Experiments have recently been made with the object of demonstrating the recoil of the emitting atom due to the ejection of a photon in a definite direction. For this purpose a narrow beam of sodium atoms was irradiated with light corresponding to the resonance line. The result was an appreciable broadening of the beam, which may be interpreted as due to the lateral recoil of the atoms as they re-emit the light. The magnitude of the broadening effect appears to agree with that to be expected on theoretical grounds.

Doppler Effect and Compton Effect.—It is interesting to consider the Doppler effect from the point of view of the corpuscular theory of light, for it is then seen to be quite analogous to the Compton effect. In the treatment which follows no account will be taken of the variability of mass with velocity.

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* Ger. *Nadelstrahlung.*

Let v_1 and Mv_1 be the initial velocity and momentum of the atom respectively, the corresponding quantities after emission being v_2 and Mv_2 (see fig. 20). Let the emission of the light quantum be in the perfectly definite direction towards the observer at A, so that the atom is given a momentum in the opposite direction. As experiment shows (p. 220), the relative motion of the atom with respect to the observer produces a Doppler effect, i.e. the frequency measured by an observer at rest at A is not the frequency ν which would be observed for an atom at rest, but has a different value ν'. According to the principle of the conservation of energy, we may equate the energies before and after the emission process, i.e. if W_1 and W_2 are the energies of the atom in the stationary states before and after emission respectively, we may write

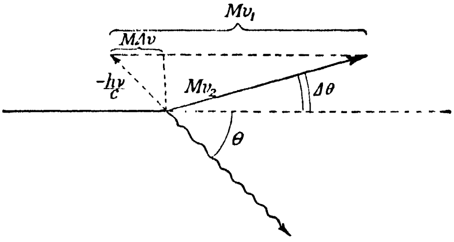

Fig. 20.—Corpuscular interpretation of the Doppler effect

$$W_1 + \tfrac{1}{2}Mv_1^2 = W_2 + \tfrac{1}{2}Mv_2^2 + h\nu',$$

or

$$\tfrac{1}{2}M(v_1^2 - v_2^2) = h\nu' - (W_1 - W_2).$$

But $h\nu = W_1 - W_2$. Hence, writing $\nu' - \nu = \Delta\nu$ and $v_1 - v_2 = \Delta v$, we have

$$h\Delta\nu = \tfrac{1}{2}M(v_1^2 - v_2^2) = \tfrac{1}{2}M\Delta v(v_1 + v_2) = M\Delta v v,$$

where $v = \frac{1}{2}(v_1 + v_2)$ is the mean of the initial and final velocities. By the principle of the conservation of momentum we have in addition, approximately,

$$Mv_1 = Mv_2 + \frac{h\nu'}{c}\cos\theta,$$

or

$$M\Delta v = \frac{h\nu'}{c}\cos\theta.$$

Combining this with the equation obtained above, we have

$$\Delta\nu = \nu'\frac{v}{c}\cos\theta,$$

$$\nu' = \frac{\nu}{1 - \frac{v}{c}\cos\theta}.$$

If we regard $v\cos\theta/c$ as small relative to unity, an assumption which is justified in view of the fact that no account has been taken of the variation of mass with velocity, this equation may to a first approximation be rewritten in the form

$$\nu' = \nu\left(1 + \frac{v}{c}\cos\theta\right).$$

This is the same formula for the Doppler effect as was deduced from the wave-theory (cf. p. 219). Here it is deduced from the corpuscular point of view, the change of frequency being regarded as due to the recoil of the emitting atom as it loses a photon. Thus the present discussion is analogous to that given previously for the Compton effect.

All phenomena connected with alterations of direction can be interpreted in a similar manner, i.e. by the corpuscular theory without reference to the wave-theory. This is true, for example, of reflection, refraction, and diffraction. Thus the interference phenomena of X-rays, as obtained with crystals, can be accounted for in terms of a quantized exchange of momentum between photons and crystal lattice, the lattice constant entering into the calculations as one of the determining factors.

Axial Properties of Light Emission and Atomic Structure.—The discovery by J. Stark of the axial nature of the emission of light is an important contribution to the general problem of radiation.

The electric field of the isolated hydrogen atom possesses (at least approximately) central symmetry. The superposition of a uniform external electric field gives a resultant field having axial symmetry. Along the axis, however, the field is asymmetrical: on the one side the atomic field is strengthened, on the other side weakened, by the external field. The corresponding series lines of the heavier elements (without external field) are found to behave analogously to the Stark-effect components of the hydrogen lines. From this Stark concluded that the atomic field of these elements must have a structure analogous to that of the hydrogen atom in an external field. This structure is apparent, e.g. in the axial nature of the valency fields of atoms like carbon and nitrogen.

There is a genetic relationship between the electric field of an atom and the electromagnetic field of the light which it emits. Hence the light emitted from an atom whose field has an axial structure may be expected to show corresponding axial properties. Experiments carried out by Stark showed that this is actually the case.

In order to be able to observe the axial properties of the light, it is necessary to orient the emitting atoms in a definite manner; otherwise the emission takes place in all directions and only natural light is observed.

For the purpose of directing the emitting atoms Stark made use of the so-called "axial effect of canal rays". This is the orientation effect observed when canal rays are passed through a gas. Whenever a canal-ray particle strikes or passes close to a gas atom, the latter exerts a directing force upon it. Hence the canal-ray atoms are all oriented in the same manner.

Under these circumstances the light emitted by the oriented canal rays is found to be polarized. This is true both for atoms in motion and for atoms at rest. The quantity

$$\frac{I_p}{I_s} - 1,$$

where I_p and I_s are the intensities of the components polarized parallel and normal to the canal-ray direction respectively, is not of the same sign for all lines. The sign differs for different elements and for different series.

In addition to this polarization, the light emitted by the canal rays shows axial properties as regards intensity. The intensity of emission in the forward sense along the direction of the canal rays is not the same as that in the backward sense (STARK, 1910). In the actual experiments the observations are not made in the direction of the canal rays, but at various angles. The intensity ratio $I_{45^\circ}/I_{135^\circ}$ is then a measure of the magnitude and direction of the axial nature of the light. The direction in the case of emission from atoms at rest may be opposite to that in the case of atoms in motion.

The atoms can also be oriented axially by means of an applied electric field normal to the direction of motion of the canal rays. Interesting relationships are then observed in the relative intensities of the components in the longitudinal Stark effect. Thus, for example, the ratio of the intensity of a component displaced towards the red to that of the corresponding component displaced towards the violet is found to be less than unity for all the hydrogen lines of the Balmer series hitherto investigated, the emission being in the same sense as the electric field. This ratio is also less than the corresponding ratio when the emission is in the opposite sense.

The polarization of characteristic X-radiation, mentioned on p. 58, also indicates that the emission must be axial in character, i.e. must deviate from the classical assumption of spherical symmetry.

D. THE WAVE PROPERTIES OF THE ELECTRON

9. Interference Effects with Electrons.

Some features of the interaction of moving electrons with matter have already been discussed in Chapter I (p. 33). All the phenomena dealt with so far have been in harmony with the theory that electrons are minute corpuscles spinning about their own axes. Yet, just as radiation (previously regarded as consisting of waves) has been found to have properties which are best accounted for by a corpuscular theory (see p. 117 *et seq.*), so also in the interaction of electrons with matter phenomena have been observed which are best accounted for by a wave-theory of electrons. Thus moving electrons are found to show interference effects such as are usually regarded as characteristic of waves. From the effects it is possible to ascribe a definite wave-length to the electrons in question.

Historical.—The first indications of effects of this sort were observed by Davisson and Kunsman in 1923, but no special attention was paid to them at the time. The first definite evidence of the wave-nature of electrons was supplied in 1927 by the experiments of Davisson and Germer on the reflection of electrons at the surface of single crystals of nickel. These experiments attracted great interest in view of the fact that three years previously De Broglie had predicted the possibility of such effects from purely theoretical considerations. De Broglie's formulæ were found to be in agreement with the experimental measurements.

Diffraction of Electrons by a Lattice.—The undulatory nature of light is deduced from interference phenomena. One of the simplest methods of determining wave-lengths depends on diffraction effects produced by a grating. In 1928 Rupp succeeded in showing that electrons incident on ruled metal gratings exhibit entirely analogous diffraction effects.

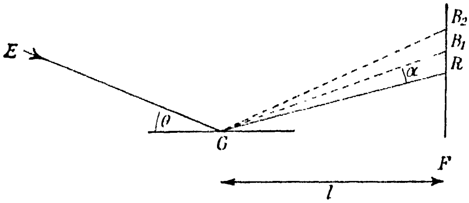

Fig. 21.—Diagram of the experimental apparatus for investigating the diffraction of electrons by a grating (angles greatly exaggerated).

The beam of electrons originating at E (fig. 21) strikes the metal plate G at the very small angle θ. The metal plate is ruled in parallel lines (say 1300 per centimetre). The electrons are reflected so as to fall on a photographic plate placed, as shown in the figure, at a distance $GF = l$ from the point of incidence of the electrons upon the grating. On the assumption that a definite wave-length λ can be ascribed to the electrons, we shall get (in addition to the regularly reflected maximum at R) a series of diffraction maxima B_1, B_2. Then, if the angle RGB_1 is α, a simple argument exactly similar to that for the corresponding optical case gives $\cos\theta - \cos(\theta + \alpha) = n\lambda/d$, or, for small values of θ and α,

$$n\lambda = \tfrac{1}{2}d\alpha(\alpha + 2\theta),$$

where d is the grating constant and n the order of the diffraction maximum.

In this method d and α are known, while λ and θ (the latter on account of its smallness) are to be found. Hence in order to determine

λ absolutely it is necessary to measure the position of at least two diffraction maxima. The conditions which must be fulfilled if the experiment is to succeed are as follows: (1) the grating must be of metal, so that surface charges may be avoided; (2) the electron beam must be subjected to a longitudinal magnetic field in order to keep it sufficiently sharply defined; and (3) the surface of the grating must be previously freed from adsorbed gases by bombardment with fast electrons. The experimental arrangement is shown diagrammatically in fig. 22. Typical experimental results are reproduced in fig. 23. Two maxima are seen in addition to the directly reflected maximum.

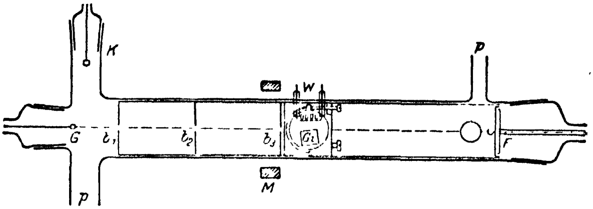

Fig. 22.—Diagram of apparatus for investigating the diffraction of electrons by a grating (after Rupp)

K, cathode; G, incandescent wire (second cathode); *b*, screens with small holes; Gi, grating; W, incandescent wire for bombarding the grating with electrons for the purpose of cleaning it; F, photographic plate.

[From *Ergebnisse der exakten Naturwissenschaften*, Vol. IX (Springer, Berlin).]

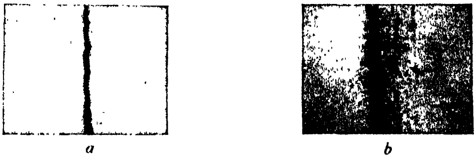

Fig. 23.—Diffraction of electrons on reflection (after Rupp)

a, without grating; *b*, with grating (150 volts). The directly reflected beam is on the left. To the right are two orders of diffraction.

[From *Ergebnisse der exakten Naturwissenschaften*, Vol. IX (Springer, Berlin).]

In these experiments the angle θ was found to be about 10^{-3}. The wave-lengths were found to be 1·5 Å. for 70 volts, 1·0 Å. for 150 volts, and 0·7 Å. for 310 volts accelerating potential. Thus the wave-lengths ascribable to these cathode rays (moving electrons) are of the same order of magnitude as those of X-rays, and decrease with increasing electron velocity. There can be no doubt that the diffraction effects are produced by electrons, because the diffraction pattern can be displaced by the action of a magnet. This shows that the effects cannot arise from electromagnetic waves.

De Broglie's Hypothesis.—In 1924, before effects of the kind referred to above were known experimentally, De Broglie in his doctorate thesis put forward the hypothesis that a wave-motion can be associated with every mass in motion. This idea was suggested to him by the analogy which exists between one of the fundamental laws of mechanics, the so-called principle of least action, and one of the fundamental laws of optics, Fermat's principle (Vol. IV, pp. 221 and 222). The former principle states that the path described between the points A and B by a massive particle under the influence of forces is such that the line-integral of the mechanical velocity v is a minimum (or has an extreme value). This may be expressed as follows:

$$\int_{A}^{B} v\,ds = \text{minimum},$$

where ds is the element of path. As was shown by **Maupertuis** and **Euler**, the fundamental equations of mechanics can be deduced from this principle. Fermat's principle, on the other hand, states that the optical path of a ray of light between two points A and B is such that the time taken is a minimum (or has an extreme value). This may be written in the form

$$\int_{A}^{B} \frac{ds}{u} = \text{minimum},$$

where u is the wave velocity. We see that the two fundamental principles are formally analogous, the mechanical velocity v on the one hand corresponding to the reciprocal of the wave velocity u on the other.

In order to obtain a connexion between moving mass m and wave, **De Broglie** as a pure hypothesis equated the mechanical momentum of the mass (namely, mv) to the momentum h/λ (see p. 224) of the waves associated with it, i.e. he put

$$\frac{h}{\lambda} = mv \quad \text{or} \quad \lambda = \frac{h}{mv}.$$

In applying these equations to electrons it is convenient to make use of the volt-velocity $U = \frac{1}{2}mv^2/e$ instead of the mechanical velocity v. Substituting the known values of e, m, and h, we obtain

$$\lambda = \sqrt{\frac{150}{U}} \times 10^{-8} \text{ cm.},$$

where U is measured in volts.

It follows that electrons with a velocity of 150 volts are associated with a wave-length of 1 Å. Actually the wave-lengths obtained from the diffraction experiments described above agree within the limits of experimental error (a few per cent) with the values anticipated from the formula. Hence it is established that moving electrons do in fact possess a quite definite wave-length, just as light does.

It must be clearly realized, however, that there is a fundamental difference between electron waves and light waves. Light waves are electromagnetic. Their velocity of propagation in space devoid of matter is $c = 3 \times 10^{10}$ cm./sec. The waves of moving electrons are of quite a different character, and their real nature is so far unknown. The velocity of propagation of their energy (i.e. their group velocity—see Vol. IV, p. 172) is equal to the mechanical velocity v of the massive particle. Now it will be shown below that the wave velocity u (phase velocity) is given by $u = c^2/v$. Hence, since v must always be less than c (p. 230), this wave velocity must always be greater than the velocity of light. For example, electrons moving with the velocity of 10^{10} cm./sec. (about 30,000 volts) must have ascribed to them a wave velocity three times that of light.

The equation $u = c^2/v$ referred to above follows from the relationship $\lambda\nu = u$, which holds for all waves, and from the energy equation $h\nu = mc^2$, which is found to hold for electron waves. Combination of these equations gives $mc^2 = hu/\lambda$. Since, in addition, $\lambda = h/(mv)$ (see above) we obtain

$$c^2 = uv.$$

We have no knowledge of the real nature of electron waves. The fact that their velocity of propagation (wave velocity) is so much greater than the velocity with which their energy is propagated (group velocity) need not cause surprise. The difference between wave velocity and group velocity has been dealt with in Vol. II (p. 222). Reference may be made in this connexion to MICHELSON's measurements of the velocity of light in carbon disulphide (see Vol. IV, pp. 219, 220).

10. Further Experiments on the Wave Properties of Electrons

Since the wave-lengths of electrons of experimentally-attainable velocities are of the same order of magnitude as those of X-rays, and since a crystal lattice constitutes a periodic array of disturbing points for electrons just as it is for X-rays, we may expect to get interference effects when electrons are allowed to fall on a crystal. One fundamental difference between electrons and X-rays must, however, be taken into account: electrons carry an electric charge and hence may be deflected by electric or magnetic fields. These deflections are greatest for electrons of lowest velocity. When slow electrons are used, the fields which exist in crystals may therefore be expected to cause appreciable deviations from the behaviour of X-rays.

Diffraction of Fast Cathode Rays by Crystals.—All the three X-ray methods, the BRAGG method, the LAUE method, and the DEBYE-SCHERRER method, find their analogues in the case of fast electrons.

Fig. 24 illustrates the principle of the experimental apparatus for making fast electrons pass through thin foils. The beam of electrons is emitted from the incandescent electrode G and, after passing through a series of small holes in screens B, falls on the thin foil F (or on a very fine powder spread over the surface of a foil). The trace received on the photographic plate P shows (in addition to the central point corresponding to direct passage of the electrons through the foil) a number of rings corresponding to the Debye-Scherrer rings obtained with X-rays. The central spot is diffuse on account of the effect discussed on p. 234. The thickness of the metal foils used lies between 10^{-6} and 10^{-7} cm. They may be prepared either by condensation upon rock salt which is afterwards dissolved away (Rupp's method) or else by sputtering upon cellulose acetate (G. P. Thomson).* If the foil is too thick no interference effects are obtained, but only a general scattering of the kind discussed in Chapter I. This is one of the reasons why the discrete rings were not observed earlier. Fig. 25 is a reproduction of the rings obtained with a silver foil. Interference effects of this kind were first observed in 1927 by Thomson and in 1928 by Rupp. It is certain that the effects are really produced by electrons, because the interference pattern is distorted when a magnet is held near the plate (see fig. 26). The pattern produced by X-rays of the same wave-length would present the same initial appearance as that produced by electrons, but would remain quite unaffected by a magnet.

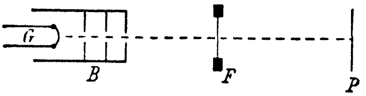

Fig. 24.—Diagram of apparatus for investigating the passage of electrons through thin foils.

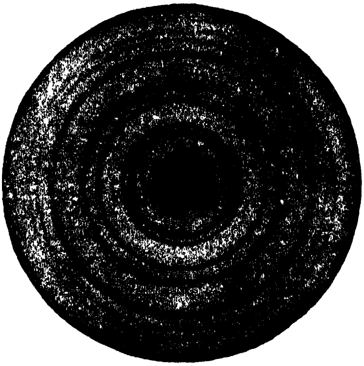

Fig. 25.—Diffraction of fast electrons (36,000 volts) by a silver foil ($\lambda = 0{\cdot}06$ Å.)

[From Mark and Wierl, *Zeitschrift für Physik*, Vol. LX (Springer, Berlin).]

Measurements upon the interference patterns obtained with electrons show that the electron waves behave quantitatively in the same way as X-rays. The same formulæ for the interference maxima apply to both, and the same value is obtained for the lattice constant of the crystal, provided that the wave-length ascribed to the electrons is in accordance with the equation already given above.

Peculiar results are obtained with thin slips of mica, which are single crystals. In this case, as is to be expected, the pattern is analogous to the Laue type of

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* Sir G. P. Thomson (1892 —), Professor of Physics, Imperial College of Science, since 1930; Nobel Prize for Physics, 1937.

X-ray pattern (see fig. 27). At higher electron densities interference effects of quite a different character appear. These are similar to the effects produced with

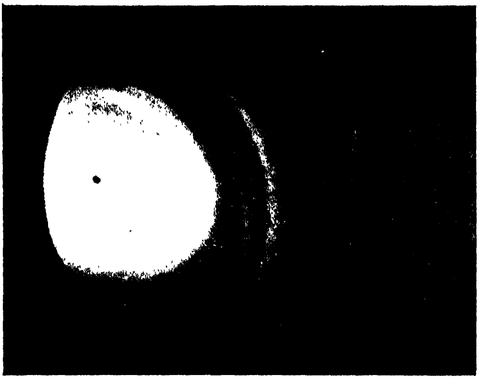


Fig. 26.—Distortion of an electron diffraction pattern by a magnet (after Thomson)

light, when a two-dimensional lattice is used. Thus under these conditions the mica loses its periodic properties in the direction of the beam—a consequence,

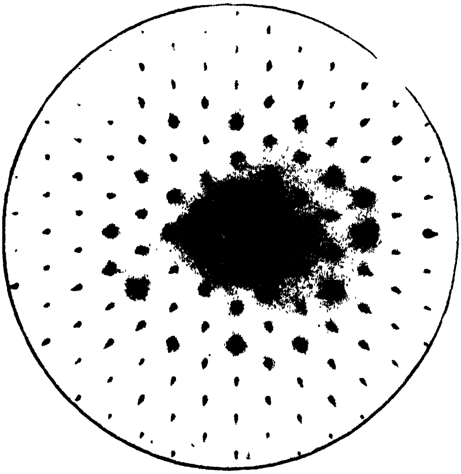


Fig. 27.—Diffraction of electrons by thin mica (45,000 volts)

[From *Jahrbuch des Forschungsinstituts der A.E.G.*, Vol. II (1930) (Springer, Berlin.]

as **Rupp** showed, of the splitting of the crystal under the intense electron bombardment. With thicker sheets of mica more complicated processes occur and patterns like that shown in fig. 28 are obtained.

Experiments with Cathode Rays of Moderately High Velocity.—The principal experiments of this kind (with electrons of a few hundred volts velocity) were carried out by Rupp in 1928. The conditions of experiment are less favourable than for fast electrons, the chief difficulties being the preparation of sufficiently thin foils, the rendering of the electron beam uniform in velocity, and the sensitization (by means of oil) of the photographic plate. Fig. 29 is a reproduction of a diffraction pattern obtained with a silver foil and electrons with a velocity of 180 volts. A method considerably simpler than photographic recording is to determine the electron distribution behind the foil by means of a collecting cage.

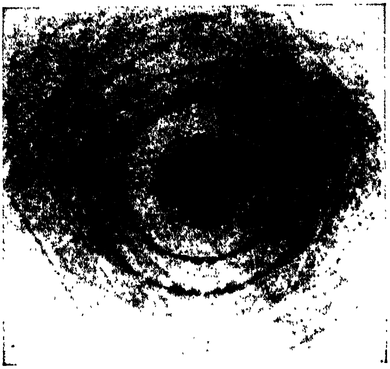


Fig. 28.—Diffraction of electrons by thicker mica ($\lambda = 0{\cdot}048$ Å.)
Twice original size

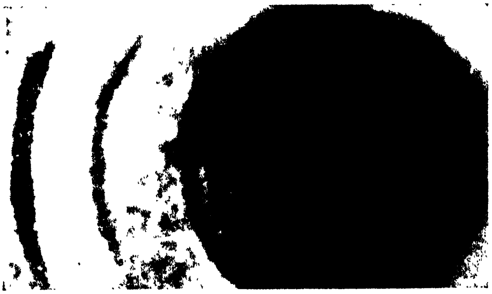


Fig. 29.—Diffraction of moderately fast cathode rays (180 volts) by silver (after Rupp)

Measurements upon the observed diffraction patterns show that they do *not* obey the X-ray formulæ. This result is due to influence of the fields of the lattice on the slow electrons.

Refractive Index and Internal Potential.—The deviations from the X-ray formulæ can be accounted for by supposing that the wave-length of the electrons, which is λ in air, assumes a different value λ_m in the interior of the metal. We may accordingly introduce a refractive index μ, defined by analogy with the optical case as $\mu = \lambda/\lambda_m$. Such an alteration of wave-length involves a corresponding change of velocity (see the equation on p. 246), which indicates that the electron is subjected to an electric field in the direction of its motion. In the case of metals μ is greater than unity; in the case of non-conducting crystals it is generally less than unity. With increasing electron velocity the value of μ approaches unity for metals. Thus on penetrating into a metal the electrons are accelerated by an electric field. If the extra velocity so imparted is E_0 (in volts), we have

$$\mu = \frac{\lambda}{\lambda_m} = \sqrt{\frac{U + E_0}{U}},$$

where U is the original volt velocity. This inner electric field is probably also the cause of the work which must be done in order to free an electron from the metal in the photoelectric effect. The so-called inner potential (in volts), as calculated from the refractive index for electrons, has the following values for different metals:

Fe	Zn	Ni	Cu	Ag	Au	Al
14	16	16	13·5	14	14	17.

Regarding the fact that μ is less than unity for non-conducting crystals, i.e. that the electrons have to overcome an opposing field, it is not possible to make any precise statement, since the opposing field might be due to electrons which had adhered to the surface.

In the diffraction patterns obtained with electrons rings are often observed which do not appear in the corresponding X-ray patterns. Their non-appearance with X-rays is due to the effect of interferences of high orders which are negligible in the case of electrons, owing to the relatively small penetration of the latter into the crystal.

Maxima are also observed with electrons at positions corresponding to half-integral orders. These are given by metals containing gases. Their cause is not yet fully understood.

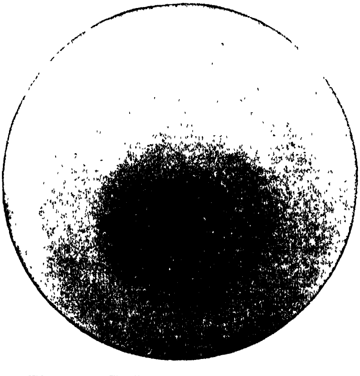


Fig. 30.—Diffraction of electrons by a beam of vapour (CCl_4; 36,000 volts)

[From *Ergebnisse der exakten Naturwissenschaften*, Vol. IX (1930) (Springer, Berlin).]

Diffraction of Electrons by Gases.—Just as in the case of X-rays (Debye, 1927), diffraction effects can be observed when electrons are made to pass through a stream of gas (Mark and Wierl, 1930). Fig 30 shows a typical ring pattern. The theory given by Debye makes it possible to determine, from the distances between the rings, the distances between the atoms in the molecule of the gas. For example, the distance between the chlorine atoms in the CCl_4 molecule is found to be 3·14 Å. The method promises to give valuable information in a number of important chemical problems.

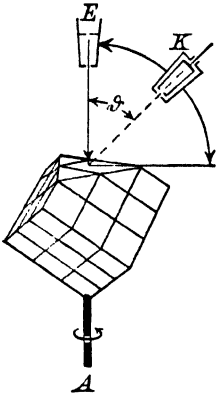


Fig. 31.—Diagram of apparatus for investigating the reflection of electrons from a face of a single crystal ((111) face).

Experiments upon the Reflection of Electrons.—The first experiments which indicated that interference effects could arise in the interaction of electrons and crystal lattices were of the reflection type (Davisson and Germer, 1927). The first method corresponds to the Laue method for X-rays (p. 63). The experimental arrangement is shown diagrammatically in fig. 31. A narrow beam of electrons from the source E is allowed to fall on the crystal. In the figure the octahedral (111) face of a cubic crystal has been chosen. The intensity of the electrons thrown back (reflected) from the crystal at various angles is determined by means of the collector K. The crystal can also be rotated about a normal to the face under investigation (variation of azimuthal angle). In this way a complete record of the distribution of the reflected electrons in space is obtained. In addition, determinations can be made for different electron velocities, as well as for different positions of the collector in space. By means of an auxiliary opposing field the collector is adjusted so as to admit only electrons which have suffered no loss of energy.

Fig. 32 shows the results of a series of measurements with electrons of different velocities, using the (111) face of a single crystal of nickel. In each polar diagram the radius vector is the intensity of reflected electrons and the angles are the corresponding θ-values (see fig. 31). The crystal is kept in one definite orientation throughout. We see that there is a very marked maximum of reflection for θ = 50° and for electrons of velocity 54 volts. This maximum is almost exactly in the spatial direction in which X-rays of the same wave-length would show an intensity maximum in consequence of interference effects produced by the crystal lattice. (The wave-length of the electrons is calculated from the formula

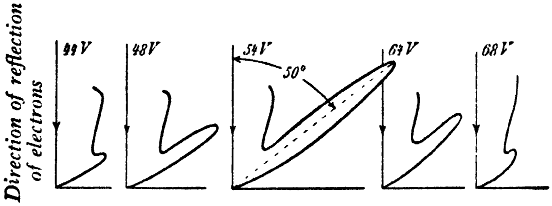


Fig. 32.—Reflection of electrons of different velocities at the (111) face of a single crystal of nickel

$\lambda = \sqrt{150/U} \times 10^{-8}$ cm., given on p. 246.) The agreement is not quite exact. The discrepancy is now known to be due to the effect of the internal field of the crystal lattice upon these relatively slow electrons (see above). When the internal potential is taken into account the discrepancies vanish. There can be no doubt that the observations here described are true interference effects, for the maximum represented in fig. 32 is not the only one which appears. Maxima are found for all the directions and all the wave-lengths for which maxima are to be expected from the theory of the corresponding X-ray case.

In another method, analogous to the Bragg X-ray method (p. 70), the electron beam is allowed to fall on the crystal at different angles, and the intensity of electron reflection at different angles is measured by means of a collector with a small aperture. A maximum is observed whenever the Bragg condition (p. 68) is fulfilled for the particular angle and wave-length (i.e. velocity) in question. This is exemplified in fig. 33, where the intensities of reflection at different angles are plotted in polar co-ordinates. Alternatively, the angles of incidence and reflection may be kept constant and the electron velocity varied. Fig. 34 shows an example of the successive maxima obtained in this type of experiment.

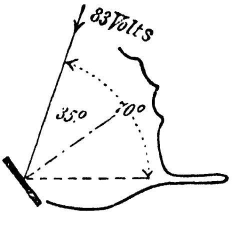


Fig. 33.—Diffraction maxima in the reflection of electrons at the (111) face of a single crystal of nickel.

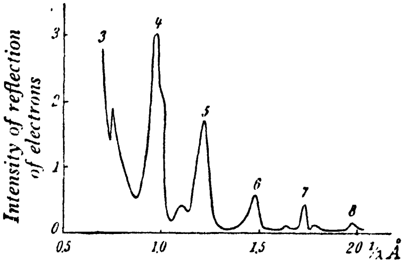


Fig. 34.—Diffraction of electrons of different velocities at the (111) face of a single crystal of nickel. Angle of incidence 10°.

In summary, we may say that the experiments on the reflection of electrons from crystal faces show that diffraction effects occur which are completely analogous to the effects for X-rays, provided that the refractive index of the crystal for X-rays is taken into account and that a wave-length is ascribed to the electrons in accordance with De Broglie's relation.

11. Variability of Electron Mass and Polarization of Electrons

Determination of the Variation of the Mass of an Electron with Velocity.—The De Broglie equation for the wave-length of electron waves involves the mass of the electron. This, however, varies with velocity, and the value of the mass used in the equation must be the value for the particular velocity in question. Conversely, the mass can be determined from accurate wave-length measurements by interference methods. By using electrons of different velocities it is thus possible to determine the variation of the mass. Determinations of this kind were carried out by Rupp, whose measurements extend up to velocities of 250,000 volts. The wave-length measurements were made by observing the diffraction rings obtained with a thin polycrystalline gold foil (see fig. 35), and using the ordinary X-ray formula. The lattice constant was determined by means of corresponding X-ray diffraction experiments. The results gave a variation of electron mass with velocity in accordance with the equation

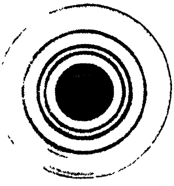


Fig. 35.—Diffraction of 220,000 volt electrons by gold (natural size).

[From *Jahrbuch des Forschungsinstituts der A.E.G.*, Vol. III (1933) (Springer, Berlin).]

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}},$$

which has already been given on p. 228 above. From this may be deduced the following formula for the wave-lengths of electrons at the higher velocities:

$$\lambda = \sqrt{\frac{149{\cdot}55}{\mathrm{U}}}\,\frac{10^{-8}}{\sqrt{1 + 9{\cdot}836 \times 10^{-7}\mathrm{U}}}\ \mathrm{cm.},$$

where U is the volt velocity. The correction due to the factor $1/\sqrt{1 + 9{\cdot}836 \times 10^{-7}\mathrm{U}}$ amounts to about 5 per cent for a velocity of 100,000 volts and to as much as 11 per cent for 250,000 volts.

Accurate determinations of the wave-lengths of slow electrons have been carried out by Bühl, who found that the variation with velocity is in good agreement with the De Broglie relation. This relation is accordingly capable of accounting for observed results for electron velocities ranging from 0·02 c up to 0·75 c, where c is the velocity of light (3×10^{10} cm./sec.).

The equation of De Broglie may be written in the form

$$\frac{h}{e} = \frac{\lambda v}{\frac{e}{m_0}\sqrt{1 - \frac{v^2}{c^2}}}.$$

Hence, since e/m_0 is known very accurately (Vol. III, p. 321), it is possible to determine the value of h/e very accurately from diffraction and velocity measurements. Rupp has carried out measurements of this kind and found that $h/e = 4{\cdot}1366 \times 10^{-8}$ erg-sec. per coulomb ± 3·1 per mille. The values obtained by other methods, using the equation $h\nu = e\mathrm{U}$, are: (1) $4{\cdot}1227 \times 10^{-8}$ from the ionization potential of mercury; (2) $4{\cdot}115 \times 10^{-8}$ from the short-wave X-ray limit; and (3) $4{\cdot}1088 \times 10^{-8}$ from the photoelectric effect in metals (p. 121).

Polarization Phenomena with Electron Beams.—We have already seen (p. 209) that it is necessary to ascribe a spin to the electron. This indicates that the electron must possess a definite axis. Hence we may expect that the electron waves will show phenomena corresponding to the polarization of light. The electrons of a beam are oriented in two opposite directions by passage through a magnetic field (p. 207). Thus under these conditions we have two independent trains of electron waves. In the case of light two trains of waves cannot interfere when their planes of polarization are at right angles. In the case of the electrons the angle between the two spin directions is 180°.

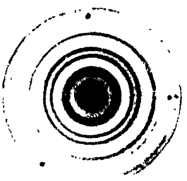
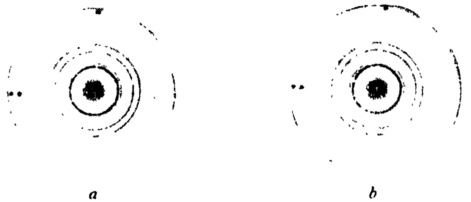


Fig. 36.—Asymmetrical intensity distribution in the diffraction of electrons (250,000 volts) by gold foil, arising from electron polarization.

[From *Jahrbuch des Forschungsinstituts der A.E.G.*, Vol. III (1933) (Springer, Berlin).]

A simple method of producing polarized light is by reflection at a mirror. Analogous investigations have been carried out by Dymond and by Rupp with electrons reflected at 90° from a gold foil. In one set of experiments the diffraction effects were observed; in another the distribution of intensity on reflection from a second surface was determined, as in the Nörrenberg polarization apparatus for ordinary light (Vol. IV, p. 227). In the first set of experiments it was found that there are intensity differences in the diffraction patterns, depending on whether the electron beam had previously been reflected at 90° by the gold foil or not. This can be seen by comparing figs. 35 and 36. In fig. 35 an ordinary beam of electrons was used and the intensity of the rings is uniform. In fig. 36 a beam of previously-reflected electrons was used and the rings show a greater intensity on one side. The effect can be seen best for the outer rings, the maximum of intensity being marked in the figure by two dots close together.



a *b*

Fig. 37.—Rotation of the symmetrical intensity distribution by means of a longitudinal magnetic field. (220,000 volts; $l = 5$ cm.)

[From *Jahrbuch des Forschungsinstituts der A.E.G.*, Vol. III (1933) (Springer, Berlin).]

This effect must be connected with the axial properties of the electrons (i.e. with properties analogous to polarization), because the intensity distribution is turned through a definite angle when the electrons are made to pass through a longitudinal magnetic field.

It should be mentioned, however, that careful experiments by G. P. Thompson, and by Dymond, showed at most only a small fraction of the polarization to be expected from the theory.

Electron Microscope.—The path of an electron beam through an electric or magnetic field is closely analogous to that of a light beam through a lens. By suitable adjustment of potentials it is possible to bring the beam to a focus and to form images. On account of the smallness of λ (p. 254), electron microscopes now in use have a resolving power 50 to 100 times that of an ordinary microscope.

E. The Wave Properties of Material Particles

12. Diffraction of Atomic Rays by Crystal Lattices

The De Broglie relation is applicable to any mass. In particular, it may be applied to light. Even in the case of atoms (and perhaps also assemblages of atoms) it appears from experimental results that certain phenomena are governed by the wave-length ascribable to the total mass. Again, as with electrons, the wave nature of matter is apparent in diffraction effects. Ellet and Olson observed such effects in 1928 in studying the reflection of beams of cadmium and mercury atoms from rock salt. They were able to show that the reflected atomic rays were always uniform for one direction, but that the magnitude of the velocity (and hence the wave-length ascribable to the rays) depended upon the angle of reflection. This result is quite analogous to that for X-rays, where out of an incident beam containing a continuous range of wave-lengths only that wave-length is reflected which satisfies the Bragg relation for the particular angle of reflection in question.

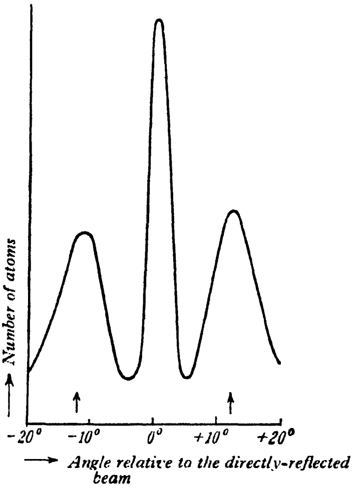


Fig. 38.—Presumed diffraction effects in the reflection of helium atoms by lithium fluoride. Angle of incidence 18½° (after Estermann and Stern).

The experiments of Estermann and Stern (1930) are more convincing. In the reflection of atomic rays at crystal faces they obtained (in addition to the regularly-reflected beam) maxima of intensity corresponding to the orders of diffraction (see fig. 38).

Clear proof of the wave nature of protons is provided by the experiments of Rupp (1932), in which protons accelerated by a potential of 200,000 volts were shot through gold foils. Diffraction rings were obtained, just as in the experiments with electrons referred to on p. 252.

In the case of protons the De Broglie relation is $\lambda = h/(Mv) = (28{\cdot}6/\sqrt{U}) \times 10^{-10}$ cm., U being measured in volts. The diffraction rings satisfy the X-ray type of formula, namely, $n\lambda = 2d \sin \frac{1}{2}\varphi$. On account of the smallness of λ, φ is also very small, and hence the photographic plate must be placed at a large distance (3·5 metres) from the foil. The beam of protons is produced in a special part of the apparatus, a potential of 2000 volts being used. The canal-ray particles H^+ and H_2^+ passing through the perforated cathode are then accelerated in another part of the apparatus by the potential of 200,000 volts, after which they pass through a narrow passage 20 cm. long which has apertures about 5 mm. long and 0·1 or 0·06 mm. in diameter at either end. Finally the proton beam is incident upon the gold foil and then upon the photographic plate. Fig. 39 shows a pattern of diffraction rings obtained in this way. The actual record has been intensified in reproduction so as to make the rings clearer. The figure is twice the original size. The wave-length calculated from the diffraction pattern is found to agree within one or two per cent with that calculated from the De Broglie relation ($\lambda = 6{\cdot}40 \times 10^{-12}$ cm.).

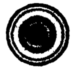


Fig. 39. — Diffraction of protons (about 200,000 volts) by gold foil (after Rupp; about twice original size).

(From *Zeitschrift für Physik*, Vol. LXXVIII (1932) (Springer, Berlin).)

Diffraction rings belonging to the H_2^+ particles present in the beam were not observed.

F. THE WAVE-MECHANICAL MODEL OF THE ATOM

13. The Schrödinger Equation

The recognition of the wave nature of the electron has led to the construction of a new atomic model, the foundations of which were laid by Schrödinger in 1925.

Wave Representation of an Orbital Electron.—The following simple argument will show that the wave theory of the electron is capable of forming a suitable basis for an atomic model.

The equation for the displacement S in a sinusoidal wave of amplitude A progressing in the direction of increase of the distance co-ordinate s has been given at the bottom of p. 220 of Vol. II; it is

$$S = A \sin\left[2\pi\left(\nu t - \frac{s}{\lambda}\right)\right].$$

Some of the symbols have been altered in writing the equation here, and the frequency ν has been introduced instead of the reciprocal of the periodic time T. The wave-length as usual is denoted by λ.

We shall now apply this wave equation to the case of an electron which, according to the Bohr model, is circulating in an orbit about the nucleus of an atom. Let us consider a circular orbit for simplicity, assuming it to be so small that the wave-train associated with the electron extends at least right round the circumference. Thus the distance s in the wave equation is the length of arc measured round the circular orbit. The angle $2\pi\left(\nu t - \frac{s}{\lambda}\right)$ occurring in the equation is called the phase angle ϕ. At a given moment ($t =$ constant) the difference of phase $d\phi$ between two points a distance ds apart is clearly

$$d\phi = -2\pi\frac{ds}{\lambda}.$$

The phase difference between two points 1 and 2 at a finite distance apart on the orbit is therefore

$$\phi_2 - \phi_1 = -\frac{2\pi}{\lambda}\int_1^2 ds.$$

Imagine the point 1 as remaining fixed, while the point 2 is moved farther and farther from it round the orbit. Eventually 2 will have been moved right round the circle and will reach the point 1 again. The phase difference introduced by this complete circuit of the orbit is

$$-\frac{2\pi}{\lambda}\oint ds,$$

the circle through the integral sign indicating that the integration extends once round the orbit. Now if the state is to be stationary, the quantity S, as also its time derivative, must have a single definite value at each point. Hence when the point 2 becomes coincident with the point 1, we must have

$$\sin\phi_2 = \sin\phi_1,$$

and

$$\cos\phi_2 = \cos\phi_1,$$

i.e. $\phi_2 - \phi_1$ must be an integral multiple of 2π. This may be written in the form

$$\frac{2\pi}{\lambda}\oint ds = 2\pi n,$$

i.e.

$$\oint ds = n\lambda.$$

Thus only those circular orbits are permitted for which the circumference is a whole number of wave-lengths.

The momentum G associated with the waves is given by the equation

$$G = \frac{h}{\lambda}.$$

Combining this with the above relation and substituting $\oint ds = 2\pi r$, where r is the radius of the orbit, we obtain

$$2\pi r G = nh.$$

Now rG is the angular momentum J. Hence we have finally

$$J = \frac{nh}{2\pi}.$$

In words: *Only those circular orbits are permitted for which the angular momentum is an integral multiple of $h/(2\pi)$.*

But this is just the quantum condition postulated in connexion with the Bohr atomic model. It is here seen to follow simply from the concept of electron waves.

Treatment of the problem in the above simple fashion can only serve to give a first insight into the kind of relationships involved. Actually the wave system is three-dimensional, and further analysis is necessary in order to prove that the more general theory is in accord with observation. However, even the foregoing simple argument indicates that the wave theory is a most promising line to follow up and that important results may be confidently expected from the method which treats the discrete stationary states of an atom in much the same way as the discrete modes of vibration of a stretched string subject to given boundary conditions.

The underlying idea of the wave-mechanical treatment of the atom is to regard the different stationary states as different proper modes of vibration (in general very complicated) of a certain quantity whose nature we regard for the time being as unknown. The wave-length involved is determined by the De Broglie relation. Just as a mechanical system subjected to boundary conditions (e.g. a string fixed at its ends, or a membrane fixed at its edge) can only assume certain discrete modes of vibration, so the atomic system is regarded as subject to certain boundary conditions and therefore capable of assuming only certain discrete modes of vibration, i.e. the stationary states. The problem, so far as its mathematical discussion is concerned, is to describe the vibrations by means of equations of the kind used in the classical case in which a continuous medium is assumed. In this connexion it is important to realize clearly that the medium mathematically introduced in this way into the theoretical discussion of the atom need not have any real existence. It is essentially a mathematical concept, just as the motions in phase space discussed on p. 188 are not real motions, but only mathematical concepts associated with real motions. We shall see, however, that in certain cases it is in fact possible to ascribe a physical meaning to the quantity involved in the wave motion.

Wave Equation.—For any train of waves we have $\lambda\nu = u$, where u is the velocity of propagation. Substituting in the wave equation

$$S = A \sin\left[2\pi\left(\nu t - \frac{s}{\lambda}\right)\right]$$

given on p. 257, we obtain the slightly different form

$$S = A \sin\left[2\pi\nu\left(t - \frac{s}{u}\right)\right].$$

This equation refers to the particular case in which the wave form is sinusoidal. In general a quantity S whose form is propagated with velocity u in the s-direction may be any function (say the function F) of the variable $(t - s/u)$. Thus the general wave equation, of which that given above is a particular case, is

$$S = F\left(t - \frac{s}{u}\right).$$

It is not difficult to see the meaning of this equation. Let us fix our attention on the point defined by one particular value of s. The value of S at this point at the time $(t + 1)$ is

$$\begin{aligned} S(t+1, s) &= F\left(t + 1 - \frac{s}{u}\right) \\ &= F\left(t - \frac{s - u}{u}\right) \\ &= S(t, s - u). \end{aligned}$$

Thus we see that the value of S at any point and at any instant is the same as it was one second earlier at a point a distance u farther back. In other words, the form of S is propagated in the s-direction with the velocity u.

By differentiating the equation

$$S = F\left(t - \frac{s}{u}\right)$$

twice with respect to t, we obtain

$$\frac{\partial^2 S}{\partial t^2} = F'',$$

where F'' represents the second differential coefficient of F with regard to $\left(t - \frac{s}{u}\right)$. Similarly, by differentiating twice with regard to s, we obtain

$$\frac{\partial^2 S}{\partial s^2} = \frac{F''}{u^2}.$$

The last two equations can be combined to give

$$\frac{\partial^2 S}{\partial t^2} = u^2 \frac{\partial^2 S}{\partial s^2}.$$

This is the differential equation of wave motion. It applies to the one-dimensional case in which the waves are propagated in the s-direction only. In the three-dimensional case, in which the waves spread out through space, we have to take the x-, y-, and z-directions into account. The form of the differential equation obtained is similar to that for the one-dimensional case, namely

$$\frac{\partial^2 S}{\partial t^2} = u^2\left(\frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2}\right).$$

This is often written

$$\frac{\partial^2 S}{\partial t^2} = u^2 \Delta S,$$

where ΔS is an abbreviation for $\frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2}$.

The Schrödinger Wave Equation.—In the wave theory of the atom a stationary state is regarded as a mode of vibration under certain boundary conditions. We shall consider the case of a single particle, e.g. an electron. If we assume that the displacement S at any point is a sine function of the time t, we may write

$$S = \psi \sin 2\pi\nu t,$$

where ν is the frequency and ψ the amplitude at the point in question. The value of the amplitude depends upon the particular point chosen, i.e. ψ is a function of the space co-ordinates. By differentiation we obtain

$$\frac{\partial^2 S}{\partial t^2} = -4\pi^2\nu^2\psi \sin 2\pi\nu t.$$

In the same way

$$\frac{\partial^2 S}{\partial x^2} = \sin 2\pi\nu t \frac{\partial^2 \psi}{\partial x^2}.$$

Exactly similar expressions hold for $\frac{\partial^2 S}{\partial y^2}$ and $\frac{\partial^2 S}{\partial z^2}$. If we substitute these expressions in the differential wave equation given above, namely

$$\frac{\partial^2 S}{\partial t^2} = u^2 \Delta S,$$

we obtain

$$\Delta\psi + \frac{4\pi^2\nu^2}{u^2}\psi = 0.$$

Now De Broglie's relation states that

$$\frac{u}{\nu} = \lambda = \frac{h}{mv}.$$

Substituting this in the last equation, we have

$$\Delta\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0.$$

Finally we may put

$$mv^2 = 2E_{\text{kin.}} = 2(W - E_{\text{pot.}}),$$

where W is the total energy and $E_{\text{kin.}}$ and $E_{\text{pot.}}$ are the kinetic and potential energies respectively. This gives finally

$$\Delta\psi + \frac{8\pi^2 m}{h^2}(W - E_{\text{pot.}})\psi = 0.$$

This, the so-called SCHRÖDINGER wave equation, forms the foundation of the wave-mechanical treatment of the problem of a moving particle.

The equation represents a vibration in three-dimensional space—in the mechanical case the propagation of elastic waves of a certain frequency in a non-uniform medium whose density at any point is proportional to $8\pi^2 m(W - E_{\text{pot.}})/h^2$. This density is greatest for negative values of $E_{\text{pot.}}$, i.e. (returning to the atomic model) at those regions towards which the electron is attracted. The optical analogue is the propagation of a ray in a medium of variable refractive index (cf. Vol. IV, p. 107).

In the case of i particles the wave equation assumes the form

$$\sum_i \frac{\Delta_i\psi}{m_i} + \frac{8\pi^2}{h^2}(W - E_{\text{pot.}})\psi = 0.$$

This no longer represents a vibration in ordinary three-dimensional space, but in $3i$-dimensional space. No doubt it should be possible to represent such vibrations by a three-dimensional picture, i.e. to find, even in the most complicated cases, a three-dimensional model, the mathematical description of which is the wave equation and its solutions. So far no attempt has been made to do this, so that for the time being a direct spatial interpretation can be given only when there is a single moving particle (e.g. in the case of a fixed nucleus and one electron).

The equations given above have the following remarkable property. If certain definite boundary conditions are prescribed (in the acoustic case, for example, the definite boundaries of a stretched string or of a plate, the positions of clamping, &c.) a physically significant solution is only obtainable when the parameter (the energy in the above formulation) has certain definite values. By a physically significant solution we mean one which is everywhere single-valued, finite, and continuous. In the acoustic case this property of the equation finds expression in the fact that the system can only perform certain so-called proper vibrations. The special values of the parameter for which a physically significant solution is possible are called the **proper values** (Ger. *Eigenwerte*) of the differential equation, and the corresponding solutions are called **proper functions** (Ger. *Eigenfunktionen*).*

The property of the differential equations just referred to may be illustrated by two examples which have an important bearing on the applications which follow. The equation

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* The original German terms are frequently used in English, as well as the hybrids *eigen-value* and *eigen-function*. The terms *characteristic value* and *characteristic function* are also sometimes found.

$$\frac{d^2y}{dx^2} + (A - x^2)y = 0$$

has a solution of the form $y = e^{-\frac{1}{2}x^2}$ when A takes the value unity. This can be seen by differentiating twice. We have

$$\frac{dy}{dx} = -xy; \quad \frac{d^2y}{dx^2} = -x\frac{dy}{dx} - y = y(x^2 - 1),$$

i.e.

$$\frac{d^2y}{dx^2} + (1 - x^2)y = 0.$$

A further solution is $y = 2xe^{-\frac{1}{2}x^2}$, when $A = 3$. This again can easily be verified by differentiating twice. The general form of the solutions is

$$y = He^{-\frac{1}{2}x^2},$$

where H can have the following values:

$H_1 = 1$ when $A = 1$; $H_2 = 2x$ when $A = 3$; $H_3 = 4x^2 - 2$ when $A = 5$; $H_4 = 8x^3 - 12x$ when $A = 7$; $H_5 = 16x^4 - 4x^2 + 12$ when $A = 9$, and so on.

These values of H are the so-called *Hermitian polynomials*. They can be obtained from a simple expansion in series which cannot be discussed here. Thus the proper values of the problem are the odd numbers $2n + 1$ and the characteristic functions are the corresponding values of y. It can be shown that these characteristic functions are the *only solutions* of the differential equation in question which remain finite when x becomes infinitely great.

We shall now proceed to consider some special physical cases:

1. *Particle moving under the action of No Forces.*—Here we have $E_{\text{pot.}} = 0$ and $W = E_{\text{kin.}} = \frac{1}{2}mv^2$, where m is the mass of the particle and v its velocity. Hence the wave equation becomes

$$\Delta\psi + \frac{4\pi^2m^2v^2}{h^2}\psi = 0.$$

The factor $4\pi^2m^2v^2/h^2$ is a constant, so that we may write the equation in the form

$$\Delta\psi + c\psi = 0.$$

This equation can be solved for all values of c. The kinetic energy of a particle moving under the action of no forces can therefore assume any value.

2. *Linear Harmonic Oscillator* (cf. p. 187).—In this case, if the displacement is given by $x = A\sin(2\pi\nu t)$, differentiation gives

$$\frac{dx}{dt} = 2\pi\nu A\cos(2\pi\nu t)$$

$$\frac{d^2x}{dt^2} = -4\pi^2\nu^2A\sin(2\pi\nu t) = -4\pi^2\nu^2x.$$

The restoring force acting at the displacement x is therefore

$$-m\frac{d^2x}{dt^2} = 4\pi^2\nu^2mx.$$

The potential energy is given by

$$E_{\text{pot.}} = \int_0^x 4\pi^2\nu^2 mx\,dx = 2\pi^2\nu^2 mx^2.$$

Substituting this in the wave equation, we obtain

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(W - 2\pi^2\nu^2 mx^2)\psi = 0.$$

We may transform this by introducing the new variable ξ defined by $\xi = x\sqrt{b}$, where b is the constant $4\pi^2 m\nu/h$. If we make use of the fact that

$$\frac{\partial^2\psi}{\partial x^2} = b\frac{\partial^2\psi}{\partial \xi^2}$$

and write $8\pi^2 mW/h^2 = a$, the equation assumes the form

$$\frac{\partial^2\psi}{\partial \xi^2} + \left(\frac{a}{b} - \xi^2\right)\psi = 0.$$

We see that this is of the same type as the first example referred to above. The proper values are therefore

$$\frac{a}{b} = 2n + 1,$$

where n is an integer. Inserting the values of a and b, we have

$$W = (2n + 1)\frac{h\nu}{2}$$

or

$$W = (n + \tfrac{1}{2})h\nu.$$

Thus we obtain the same result as we did by the quantum theory (p. 188), but with the further refinement that the zero-point energy term $\frac{1}{2}h\nu$ is simultaneously determined. The quantization of the energy of the harmonic oscillator is here seen to follow directly from the concept of the particle as a wave, the argument being based on the idea of a continuous medium and not requiring the introduction of any such discontinuity postulates as are made in the quantum theory of p. 187.

3. *Rotator.*—We shall now consider the spatial problem of a particle moving on a spherical surface at the constant distance r from a fixed centre. As the centre is fixed, no wave need be ascribed to it, and it may be left out of consideration.

Since $E_{\text{kin.}}$ and $E_{\text{pot.}}$ are both constant, the wave equation may be written in the form

$$\frac{\Delta\psi}{r^2} + \frac{8\pi^2 m}{h^2}E_{\text{kin.}}\psi = 0,$$

where, if we take ψ to be independent of r, $\Delta\psi$ contains only differential coefficients with regard to angular co-ordinates. It is shown in the elementary theory of the functions called spherical harmonics that the solution of this equation is only possible for the proper values

$$\frac{8\pi^2 mr^2}{h^2}E_{\text{kin.}} = n(n + 1),$$

where n is an integer. Since m and r are constant, the kinetic energy must therefore be $n(n+1) \times$ constant. Introducing the value $E = \frac{1}{2}mv^2$, we have

$$\frac{4\pi^2 m^2 v^2 r^2}{h^2} = n(n+1).$$

Now mvr is the angular momentum p. Hence

$$\frac{4\pi^2 p^2}{h^2} = n(n+1)$$

or

$$p = \frac{h}{2\pi}\sqrt{n(n+1)}.$$

Thus in this case we arrive at a result slightly different from that obtained by the quantum theory (p. 190). Instead of n we now get $\sqrt{n(n+1)}$. As will be shown later, the wave-mechanical result is the one which is in accord with experimental observations (see p. 312).

Fig. 40 shows the proper functions for the first five proper values in the case of the linear oscillator. The ordinates are the amplitudes of the stationary waves

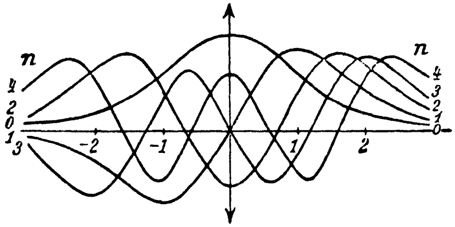

Fig. 40.—Proper functions corresponding to the first five proper values for the linear harmonic oscillator

(Vol. II. p. 234) associated with the moving mass in the different permitted energy states. The abscissæ are proportional to distances from the mean position. All the curves approach the horizontal axis asymptotically to the right and to the left. Similar curves would be obtained for the vibrations of a stretched string for which the law of propagation of waves differs for different frequencies. The same figure would also be obtained for a string if the wave velocity u were the following function of x: $u = W/\sqrt{2m(W - 2\pi^2 m\nu^2 x^2)}$, where W may assume the proper values of the equation. Thus the different permitted stationary states of the oscillator can be identified with the fundamental modes of vibration of a series of stretched strings with the properties just referred to, each proper value corresponding to a string of appropriate character.

14. Wave-mechanical Model of the Hydrogen Atom

Like the **Bohr** model, the wave-mechanical model represents a massive positive nucleus and an electron in its neighbourhood. The potential energy, reckoned relative to the state when the electron is removed to a great distance from the nucleus, is given by the Coulomb law, namely, $E_{\text{pot.}} = -e^2/r$, where r is the distance between the electron and the nucleus. The wave equation therefore becomes

$$\Delta\psi + \frac{8\pi^2 m}{h^2}\left(W + \frac{e^2}{r}\right)\psi = 0.$$

This is completely analogous to the equation for a vibrating liquid sphere in which the velocity of wave propagation at any point is given by

$$u^2 = \frac{W^2}{2m\left(W + \frac{e^2}{r}\right)}.$$

The value of u is always real for all positive values of W. In the absence of boundary conditions W can assume any positive value. The state of affairs is quite different, however, for negative values of W. SCHRÖDINGER showed that even without special boundary conditions and with merely the condition that ψ must everywhere remain finite, single-valued, and continuous, physically significant solutions are only possible (for negative values of W) when W has the discrete proper values

$$W = -\frac{2\pi^2 m e^4}{h^2 n^2},$$

where $n = 1, 2, 3, 4, \ldots$. These discrete values (W being the total energy) are seen to agree exactly with the energies of the stationary states of the hydrogen atom as deduced by the BOHR theory (p. 191). The zero for the measurement of energy is here the energy of the atom when the electron has been removed to an infinite distance from the nucleus (i.e. the energy in the completely ionized state). This accounts for the negative sign of $E_{\text{pot.}}$ above, since the electron is attracted towards the nucleus. The continuous range of permitted positive energy values corresponds to the hyperbolic and parabolic electron orbits of the BOHR model: they give rise to the continuous spectrum which is observed beyond the series limit in emission or absorption.

It should be specially noted that SCHRÖDINGER obtained satisfactory solutions without specifying any particular boundary conditions—merely by making the physically necessary assumption that the amplitude of vibration ψ must everywhere remain finite, single-valued, and continuous. We shall see on p. 268 that the region of appreciable amplitude ψ is thereby restricted to a volume corresponding to the volume of the atom as deduced from the kinetic theory of gases.

There is still a certain indefiniteness about the above solution, in that a whole set of modes of vibration is possible for each energy value. It can be shown that the wave equation, when expressed in polar co-ordinates (r, θ, ϕ), is separable into two equations, one of which contains the angular co-ordinates θ and ϕ only, while the other contains r only. It follows from the method that W does not occur at all in the first of these equations. This first equation can itself be solved only for certain proper values l, and it follows that each permitted value of the energy W may be associated with a number of proper values for the equation containing the angles only. Thus the value of W involving a particular integer n (see above) still leaves unsettled the choice of another integer l, derived from the proper values of the partial equation containing the angular co-ordinates only. The complete mathematical analysis shows that $n = n' + l + 1$, where n' is a positive integer or zero, which comes in as a proper value for the equation containing r only. Hence l may have any integral value up to $(n - 1)$ (including zero), but no others.

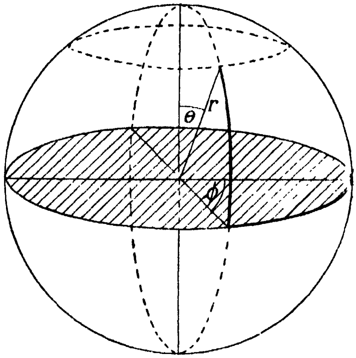

Fig. 41.—Spherical polar co-ordinates

When ψ vanishes for a certain value of r, we have a nodal sphere. When ψ vanishes for a certain value of the angle of longitude ϕ, we have a nodal plane through the origin of the co-ordinate system (see fig. 41) and cutting the surface of any sphere $r =$ constant in a meridian circle. Finally, when ψ vanishes for a certain value of the angle of colatitude θ, we have a nodal cone with its apex at the origin of co-ordinates. Only in the absence of nodal planes and nodal cones does the mode of vibration possess spherical symmetry.

The integer l referred to above determines the number of nodal surfaces (planes and cones) depending on the angular co-ordinates. Hence for each permitted value of the energy W only certain classes of vibrational modes are possible, the actual modes becoming more complicated the greater the value of the integer n (cf. the similar behaviour in the case of the linear oscillator illustrated in fig. 40, p. 265). When $n = 1$, the only value which l can assume is zero; hence there is only one kind of vibrational mode. As it possesses no nodal planes or cones, this mode is spherically symmetrical. When $n = 2$, we may have either $l = 0$ or $l = 1$. Hence for an energy value determined by the integer n (principal quantum number) there are n possible vibrational classes.

Comparison with the discussion based on the Bohr model (see p. 199) shows that both the wave-mechanical and the orbital theories lead to the same degeneracy. In order to stress the analogy, the number l was introduced on p. 199 with the property that it may assume any integral value from 0 up to $n - 1$. The different proper modes of vibration of the "liquid sphere" in the wave-mechanical model correspond to the different elliptical orbits in the Bohr model.

Stark Effect.—The degeneracy of the problem can be diminished by the application of an external field. The STARK effect has been discussed in this connexion on p. 212 in terms of the BOHR theory. The potential energy of the electron is increased by an amount eEz by the application of an electric field of strength E in the z-direction. The wave equation therefore becomes

$$\Delta\psi + \frac{8\pi^2 m}{h^2}\left(W + \frac{e^2}{r} - eEz\right)\psi = 0.$$

If we assume that the energy change due to the field is small relative to the changes which may occur in the atom in the absence of a field, then the extra energy term appearing in the wave equation may be treated as a so-called perturbation term. In these circumstances it can be shown that the equation is solvable and that each of the proper values of the unperturbed case is split up into a number of proper values of the perturbed case. The same formula is obtained as from the BOHR theory, namely

$$\Delta W = \frac{3h^2 En}{8\pi^2 me}(k_1 - k_2),$$

where ΔW is the displacement of an energy level. In the wave-mechanical model k_1 and k_2 give the number of nodal surfaces (in this case paraboloids) in the vibrating "liquid". In addition there are s possible nodal planes. The numbers k_1, k_2, and s may each assume any integral value or the value zero, provided that the equation $k_1 + k_2 + s + 1 = n$ is satisfied. This is quite analogous to the result given on p. 213.

The Possible Modes of Vibration.—As was pointed out above, to each permitted energy value W determined by the integer n there are n classes of vibration. From the number of modes of vibration in each class it follows that the total number of modes for each energy value is $\frac{1}{2}n(n + 1)$. Referring to the result given above for the STARK effect, we see that an electric field does not completely remove the degeneracy.

We shall now briefly discuss the question of the distribution of the amplitude ψ in the individual cases.

$n = 1$; $l = 0$: the proper function has no nodal surfaces. The value of ψ decreases exponentially as the distance from the centre increases, i.e.

$$\psi = Ce^{-r/a_0},$$

where $a_0 = \frac{h^2}{4\pi^2 me^2}$, which is the radius of the first BOHR circular orbit. According to the wave-mechanical model, the atom possesses perfect spherical symmetry in its lowest energy state. This result is of great significance; for we have seen (p. 210) that one of the most serious shortcomings of the BOHR atomic model is that it cannot account for the spherical symmetry of hydrogen in the ground state.

$n = 2$; $l = 0$: the vibration has one nodal sphere and has complete spherical symmetry.

$n = 2$; $l = 1$: system of vibrations having nodal planes and nodal cones, but no nodal sphere. The value of ψ decreases exponentially as r increases.

$n = 3$; $l = 0$: the vibration is spherically symmetrical and has two nodal spheres.

$n = 3$; $l = 1$: system of vibrations with one nodal sphere and nodal planes and cones.

$n = 3$; $l = 2$: vibrations with no nodal sphere and with a complicated arrangement of nodal planes and cones.

In general we may say that only those vibrations for which $l = 0$ (these occur in only one mode) possess spherical symmetry. This brings out very clearly the difference between the wave-mechanical model and the Bohr model; for in the latter $l = 0$ means the ellipse of maximum eccentricity and hence the greatest departure from circular or spherical symmetry. We shall see below, however, that something corresponding to the extreme eccentricity of these Bohr ellipses is still associated with the spherically-symmetrical vibrations of the wave-mechanical model.

Fig. 42 gives graphical representations of the *mean* value of ψ as a function of the radius r in certain cases. In these graphs, since only *mean* values of ψ are plotted, the nodal planes and cones do not appear. See also fig. 43.

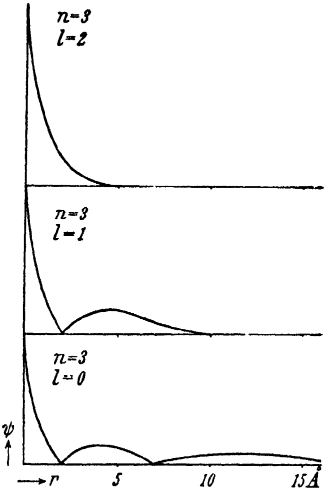

Fig. 42.—Mean values of ψ as a function of the distance from the nucleus for the hydrogen atom with $n = 3$.

Physical Interpretation of the Quantity ψ.—So far nothing has been said about the physical meaning of the vibrating quantity S or its amplitude of vibration ψ. Schrödinger has shown that a simple interpretation is possible if we relate ψ to the charge density. In simple cases the square of the amplitude ψ at any point can be regarded as a *measure of the electrical charge density* at that point. (In more complicated cases, in which ψ is complex—i.e. has an imaginary part and is of the form $a + ib$, where $i = \sqrt{-1}$—the charge density at any point is measured by the product of ψ and its conjugate complex quantity ψ^*, i.e. by $(a + ib)(a - ib) = a^2 + b^2$ instead of by ψ^2.) From the wave equation it is possible to deduce an equation analogous to the equation of continuity met with in hydrodynamics. If we interpret this as referring to the conservation of electric charge (a principle of conservation always assumed in the theory of electricity), the above physical meaning for ψ^2 (or, more generally, for $\psi\psi^*$) follows.

The sort of result to which this interpretation leads may be illustrated in the simple example of the linear oscillator. As was shown on p. 265, the wave-mechanical model of the permitted states of the system can be represented in terms of the proper vibrations of a string with special properties. In any such proper vibration the amplitude at any given point (i.e. for any given value of x) is constant and does not change with time. If now we interpret the square of the amplitude as measuring the electric charge density, it follows that the charge density at any point must also be independent of the time. This means that for any stationary state of the oscillator, no matter how great the proper energy value, the charge distribution must be static and must not vary with time. There being no movement of electric charge, *there can be no radiation of electromagnetic energy from an oscillator in a permitted energy state.* Thus we arrive quite naturally at a result which in Bohr's theory has to be assumed in the form of a postulate at variance with classical electrodynamics.

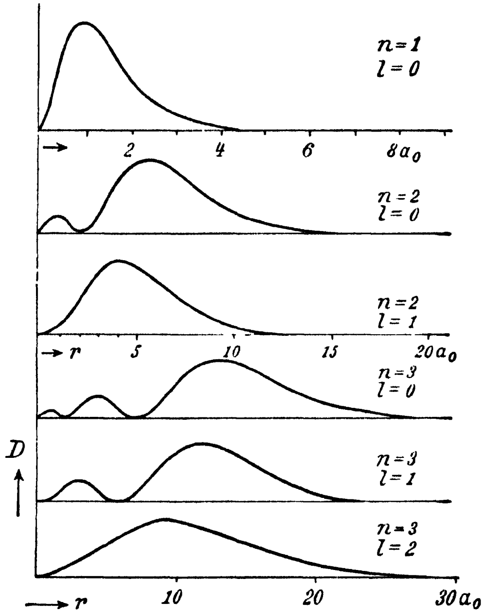

Fig. 43.—Charge distributions for different states of the hydrogen atom. The ordinates give the values of $D=4\pi r^2\psi^2$. The unit of distance r from the nucleus is $a_0=0{\cdot}53 \times 10^{-8}$ cm.

The charge distribution in the various permitted states, e.g. of the hydrogen atom, can be calculated on the above lines. Some results (after Pauling) are shown in fig. 43. In these curves the ordinates are the mean charge densities for thin spherical shells of radius r.

Hence in this representation (as in the preceding figure) the nodal spheres appear, but not the nodal planes and cones. The unit of abscissæ is a_0, the radius of the first Bohr circular orbit. The charge of the electron is spread out over the space surrounding the nucleus

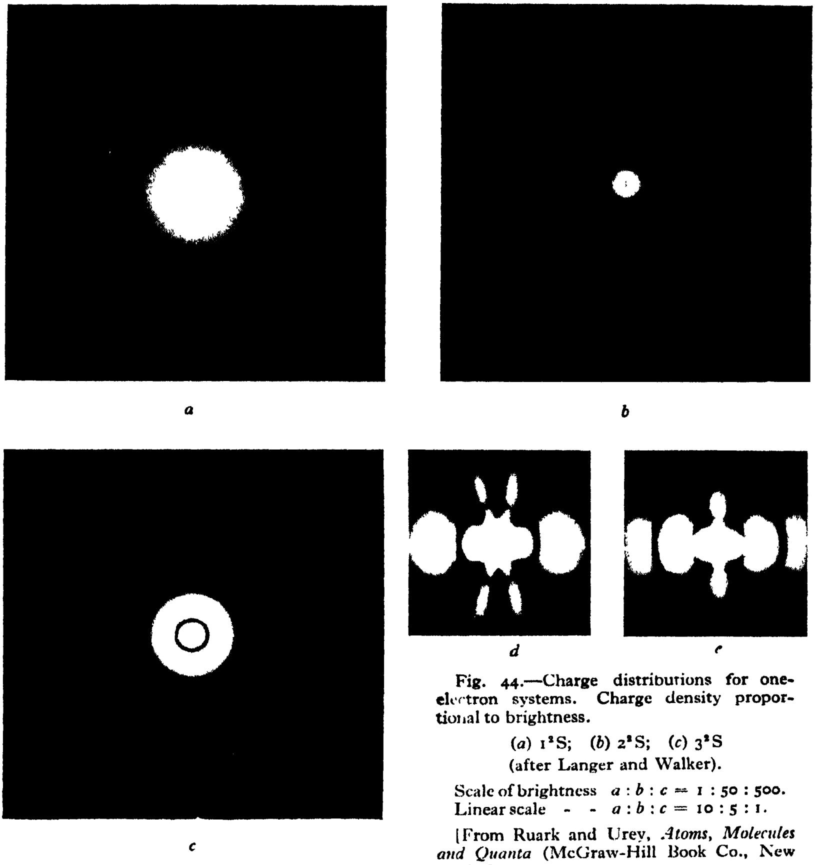

Fig. 44.—Charge distributions for one-electron systems. Charge density proportional to brightness.

(*a*) 1^2S; (*b*) 2^2S; (*c*) 3^2S (after Langer and Walker).

Scale of brightness $a : b : c = 1 : 50 : 500$.
Linear scale - - $a : b : c = 10 : 5 : 1$.

[From Ruark and Urey, *Atoms, Molecules and Quanta* (McGraw-Hill Book Co., New York).]

(*d*) 5F ($m = 0$); (*e*) 5D ($m = 0$) (after White). Linear scale - 1 : 20 relative to (*c*).

[From *Physical Review*, Vol. XXXVII, Series ii (American Institute of Physics).]

and theoretically extends to infinity. Actually we see, however, that the greatest part of the charge is concentrated within a region whose radius is approximately that derived from the Bohr theory and found experimentally in gas-kinetic and cross-section investigations. The Bohr circular orbits correspond to vibrations for which $l = n - 1$, in agreement with p. 199. The elliptical orbits correspond to charge distributions with various maxima at different distances. Attention may again be directed to the fact that, in spite of their complicated charge distributions, the wave-mechanical vibrations corresponding to **Bohr** ellipses of high eccentricity possess complete *spherical symmetry.* The property of eccentricity in the ellipse finds its analogue in the complexity of the radial distribution of charge in the wave-mechanical model.

Fig. 44 gives some pictorial representations of the charge distributions in different cases, the charge density being indicated by the brightness of the lighter parts. These pictures must be imagined as extending in three dimensions.

For another interpretation of ψ see p. 274.

15. The Wave-mechanical Theory of the Emission of Light

Schrödinger showed that a simple explanation of the process of light emission can be obtained by assuming that two permitted energy states of an atom can be excited *simultaneously.* The two corresponding vibrations of the wave-mechanical model are then supposed to be superimposed. Now we have seen in Vol. II (p. 195) that the superposition of two vibrations of somewhat different frequency gives rise to so-called *beats,* in which the amplitude waxes and wanes with a frequency which is equal to the difference between the superimposed frequencies.

If we once again interpret the square of the amplitude of vibration in the wave-mechanical model as a measure of the electric charge density, we see that when two different energy states are simultaneously excited the charge density at any given point is no longer constant, but varies periodically with the time. Hence there is an oscillation of electric charge, which must give rise to the emission of electromagnetic waves. The frequency of these emitted waves will be the beat frequency. If we write ν_L for the frequency of the light which is emitted and ν_1 and ν_2 for the frequencies of the two superimposed vibrations of the model, we have

$$\nu_L = \nu_1 - \nu_2.$$

Now according to the **De Broglie** relation the energy E of a stationary state is given by $E = h\nu$, where ν is the corresponding frequency of the wave-mechanical model. Hence we have

$$h\nu_L = E_1 - E_2.$$

Thus we arrive at the very result which **Bohr** found it necessary to introduce into his theory as a postulate.

In the case where a special axial direction is involved (e.g. in the Stark effect of the hydrogen atom the field direction is a special direction) the complete mathematical treatment shows in addition that the oscillation of electric charge may be either normal or parallel to the field, according to the nature of the wave-mechanical vibrations which are superimposed. This is the case when the respective values of the number s (see p. 268) for the two vibrations differ by 0 or 1. If the difference in the s-values is greater than 1, the calculation shows that there is no motion of electric charge. This is in agreement with the experimental observations on the Stark effect (cf. p. 211).

It may be noted also that, if account is taken of the motion of the nucleus as well as of the motion of the electron, the theory leads to a result which is in agreement with that obtained from the simpler Bohr model with a fixed nucleus, except that the mass m of the electron has to be replaced by the quantity

$$\mu = \frac{m\mathrm{M}}{\mathrm{M} + m},$$

where M is the nuclear mass. Once again (see p. 193) the conclusion from wave-mechanical theory is in excellent agreement with the facts.

The Helium Atom.—The treatment of the helium atom (a nucleus with two electrons) by the Bohr theory does not lead to a satisfactory result. The calculated energy of the ground state (relative to the energy of the ionized atom) comes out very different from the observed value. This failure of the Bohr theory was one of the chief reasons (cf. also pp. 210 and 274) for seeking a new atomic model.

The Schrödinger wave equation for the problem is at once obtained by substituting

$$\mathrm{E}_{\text{pot.}} = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}},$$

where r_1 and r_2 are the distances of the two electrons from the nucleus (which is assumed fixed) and r_{12} is the distance between the two electrons. The term $+e^2/r_{12}$ expresses the interaction between the two electrons, which will be discussed more fully later. The wave equation can only be solved approximately. If for the time being we neglect the interaction term, the proper energy value is found to be

$$\mathrm{W} = -4\mathrm{R}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right),$$

where n_1 and n_2 are positive integers associated with the respective proper values for the two electrons, which in this case can be obtained separately. This corresponds to one electron being in the n_1th Bohr orbit and the other in the n_2th. The energy of the ground state ($n_1 = n_2 = 1$), as obtained from this solution, is -8R, i.e. -106 volts. The experimentally-observed value, however, is only $-78{\cdot}5$ volts. Thus we see that we are not justified in neglecting the interaction term, which actually has a surprisingly large effect.

Wave-mechanical Resonance.—The marked effect of the interaction between the two electrons is an example of a resonance effect which is quite peculiar to wave mechanics and is due to the identity of all electrons. In Vol. II (p. 201) the vibrations of two pendulums coupled together were discussed at some length, and it was there shown that the periodic alternations of the amplitudes (due to the passage of energy backwards and forwards between the two systems) can be explained in terms of two frequencies. The mathematical treatment of the problem of an atomic system containing components of identical frequency (e.g. two electrons) shows that just the same sort of thing occurs here. We obtain new frequencies (in our case two) and a corresponding number of new energy states. Two possibilities are actually observed in the case of the helium atom for each combination of proper values—the states of the so-called *orthohelium* and *parhelium*. In the ground state, however, where $n_1 = n_2 = 1$, there is only *one* finite solution—a point to which we shall return later.

Thus the wave-mechanical theory of the electron and of matter gives the result that *whenever two identical wave-mechanical systems interact, there are two possible proper functions and two different energy values for the pair considered as a whole system.*

In this connexion it must not be forgotten that both systems extend to infinity in all directions, so that a coupling (though only a loose one) acts between systems at a great distance apart. As in the mechanical case of two coupled pendulums, when the coupling is loose the periodic energy exchange is slow, i.e. the beat frequency (and consequently the energy difference involved) is small. For an application of this see p. 388.

Statistical Interpretation of the Amplitude ψ.—The theory of the emission of light briefly outlined above is very satisfactory from many points of view. As has been pointed out, the emission of light with frequency ν_L is regarded as due to an oscillation of electric charge within the atom with this frequency. This view thus avoids all the difficulties presented by the BOHR theory and re-establishes connexion with classical electrodynamics. Yet there is a certain difficulty in supposing that the atom *simultaneously* performs two different vibrations corresponding to two different energy states. This difficulty is not a mathematical one, for the wave equation is still satisfied when the two vibrations co-exist. The physical objection to the theory can also be removed by taking account of the fact that the atom, when in the process of emitting radiation, is not in equilibrium, but is interacting with the emitted electromagnetic waves. DIRAC has shown that when this interaction is duly incorporated into the theory a satisfactory account of the process becomes possible.

From the historical point of view it is very interesting to note that a few months before the publication of SCHRÖDINGER's wave-mechanical model another theory, starting from quite different foundations, had been put forward by HEISENBERG. This theory is built up on the principle that the equations describing an atom shall contain only *observable* quantities, such as the wave-lengths or frequencies of the spectral lines, their intensities and states of polarization, and the energy levels of the atom determinable by electrical methods. The method employed by HEISENBERG in applying this principle is to replace the non-observable periodically variable co-ordinates of the electron in the atom by the totality of partial vibrations whose frequencies are equal to the frequencies of the spectral lines emitted by the atom. The spectral lines of the hydrogen atom, for instance, may be represented by means of a doubly infinite array of paired quantum numbers. The behaviour of the atom can be described in terms of such double arrays or two-dimensional schemes, the members of the array each being characterized by two indices. An array of this kind is known as a *matrix*. The mathematical handling of matrices necessitates a special matrix calculus, which had been developed many years previously. The details of the method cannot be discussed here. Suffice it to say that the results obtained are in complete agreement with those of wave-mechanics. Indeed, SCHRÖDINGER has been able to show that the two methods are mathematically equivalent, and that they differ only in the nature of the calculus used.

The above-mentioned difficulties presented by the SCHRÖDINGER theory, and especially the smearing out of the electron into a sort of "cloud", have led a number of investigators, notably BORN, to put forward another interpretation of the quantity ψ. According to this view, ψ^2 (or more generally $\psi\psi^*$) does not measure the charge density at any point, but the *probability* that an electron will be encountered at that point at any given moment. In SCHRÖDINGER'S interpretation the electron does not exist as a point charge in the atom, but is distributed over the whole of space and extends to infinity; but in the statistical interpretation, as it is called, the idea of the electron as a point charge is still maintained. In the statistical interpretation, however, we lose that readily visualized explanation of the quantum conditions which so satisfactorily avoids the difficulties raised by the BOHR model. So far as experimental evidence is concerned, the two interpretations seem to be more or less equally justified. There is nothing essentially unsatisfactory in the view that the electron only begins to have corpuscular properties when we make an observation upon it; for observation necessarily involves a disturbance of the thing observed, and in the case of the electron this may well cause a drawing together or condensation into the corpuscle with which we are familiar.

CHAPTER V

Spectral Lines and the Structure of Atoms containing more than One Electron

A. THE STRUCTURE OF LINE SPECTRA

1. General Series Relationships in the Optical Region

Like the hydrogen atom, atoms of more complicated structure give line spectra (cf. fig. 28 (p. 138), fig. 4 (p. 220), and fig. 1 (p. 278)); but these do not have such a simple structure as that of hydrogen. The conditions of excitation are also found to have a marked effect, so that the spectrum of one and the same substance may contain quite different lines when excited in different ways, e.g. in a flame, in an electric arc, or in an electric spark with or without an auxiliary capacity or inductance. The reason for this has been shown (e.g. from the observed spectral relations, see p. 289) to lie in the fact that different degrees of ionization of the atom occur in the various cases. In flames and arcs it is generally the spectrum of the neutral atom which is excited. Hence this spectrum is usually called the **arc spectrum**—even when it is not produced by an arc. The emission of the lines of the arc spectrum is thus due to transitions from excited states of the neutral atom, in the limiting case the return of an electron to the singly-charged positive ion so as to form the neutral atom again. Under more energetic conditions of excitation the spectrum contains lines due to transitions from excited states of the singly-ionized atom. These lines lie mostly in the short-wave region. If the excitation is still more energetic, lines of even shorter wave-length appear; these are due to transitions from excited states of the more highly-ionized atom, i.e. of the atom which has lost more than one electron. The spectrum of the neutral atom is indicated by writing the Roman numeral I after the symbol for the element in question, e.g. Na I. The spectrum of the singly-ionized atom is similarly denoted by II, that of the doubly-ionized atom by III, and so on. Thus, for example, investigations have been carried out upon the spectra silicon VI and vanadium V.

The number of lines in the spectra of complicated atoms is usually very great. It has nevertheless been found fairly easy to pick out *series* in the case of the elements of groups I, II, and III of the periodic table. The elements of group I (see Table I, p. 4) exhibit the simplest regularities. The farther we go to the right in the periodic table, the more complicated do the spectra become, until in the iron and platinum group it is no longer possible to make out series relationships. Even here, however, groups of lines can be found which are certainly related to one another, and considerable success has attended the investigation of their regularities. These groups are known as *multiplets*. Later (p. 335) we shall come across the explanation of this remarkable connexion between spectral character and position in the periodic table.

We shall first consider those spectra in which series relationships can be found. The discovery of these regularities forms a special branch of research. The reduction of the many lines to orderly sequences is made possible by picking out constant frequency differences and similarities of behaviour under different conditions of excitation, and by observation of line structure (sharpness, fine structure, &c., especially in the ZEEMAN effect).

Arc Spectra of the Alkali Metals.—As in the case of hydrogen (p. 183), the series can be represented by the differences between two terms, one constant and the other variable. The same series appear for all the alkali metals, so that we may consider them all together. The terms are no longer of the simple hydrogen type R/n^2, but must be written in one or other of the forms proposed respectively by RYDBERG and RITZ:

$$T = \frac{R}{(n+a)^2} \quad \text{or} \quad T = \frac{R}{[n+a+af(n,\,a)]^2}.$$

In the variable or current term, n assumes successive integral values, starting from a certain lowest value which as a rule is different for the different series. The correction term a is a constant throughout the series, and in some cases an additional RITZ correction term $af(n,\,a)$, which vanishes for the higher terms, must be taken into account.

In the main these spectra contain *four* series, known as the **principal, diffuse, sharp,** and **Bergmann or fundamental series.**

In the alkali spectra all the lines have a fine structure, being either double (*doublets*) or triple (*triplets*). The triplet structure, however, is not apparent in the spectra of the lighter alkali metals.

The different series exhibit the following relationships, which always involve the frequencies or wave numbers of the lines and not their wave-lengths.

The *principal series* is the one with the series limit of shortest wave-length (see fig. 1). The lines form doublets, the doublet separation becoming smaller as the sequence number n of the series increases, so that the limit of the series is the *same* for both components of the doublet. Thus the series limit is not double but simple. The *diffuse series* consists of doublets with a constant separation. Here, therefore, there are *two* series limits, the separation of which is equal to the doublet separation. The same is true for the *sharp series.* The diffuse series and the sharp series have *the same* limit. The *Bergmann or fundamental series* (called fundamental because the correction constant *a* in its current term is very small and the series therefore resembles that of hydrogen very closely) lies entirely in the infra-red, and the resolution of the lines has so far not been completely accomplished. The following important relationship is found to hold: *the frequency of the first member of the principal series is equal to the difference between the frequencies of the limits of the principal series and the diffuse (or the sharp) series.*

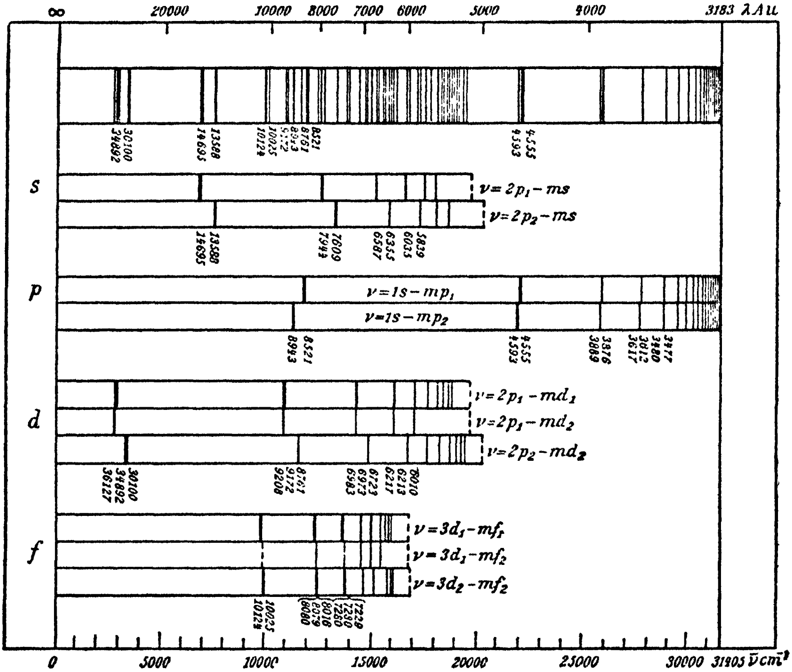

Fig. 1.—Arc spectrum of an alkali metal (Cs) and its resolution into series *s*, sharp; *p*, principal; *d*, diffuse; *f*, fundamental.

[From Grotrian, *Graphische Darstellung der Spektren*, Part II (Springer, Berlin).]

There is also a difference in the relative intensities of the doublet components. In the principal series of the alkali metals the shorter-wave component of a doublet is always the more intense, while in the diffuse and sharp series the longer-wave component is the more intense.

Fig. 1 shows how the whole spectrum (arc spectrum) of an element may be resolved into series. We may make use of the

RYDBERG formula in writing the equations for the various terms of a series, namely,

$$\bar{\nu} = \mathrm{R}\left[\frac{1}{(n+a)^2} - \frac{1}{(m+b)^2}\right],$$

in which m may take any of the values $(n+1)$, $(n+2)$, ... The symbol $\bar{\nu}$ is used to distinguish the wave-number from the frequency ν (see p. 181).

In the case of potassium, for example, we have the following relations:

Principal Series:

(*a*) $$\bar{\nu} = \mathrm{R}\left[\frac{1}{(1+0{\cdot}77)^2} - \frac{1}{(m+0{\cdot}235)^2}\right].$$

(*b*) $$\bar{\nu} = \mathrm{R}\left[\frac{1}{(1+0{\cdot}77)^2} - \frac{1}{(m+0{\cdot}232)^2}\right].$$

Diffuse Series:

(*a*) $$\bar{\nu} = \mathrm{R}\left[\frac{1}{(2+0{\cdot}235)^2} - \frac{1}{(m-0{\cdot}147)^2}\right].$$

(*b*) $$\bar{\nu} = \mathrm{R}\left[\frac{1}{(2+0{\cdot}232)^2} - \frac{1}{(m-0{\cdot}147)^2}\right].$$

Sharp Series:

(*a*) $$\bar{\nu} = \mathrm{R}\left[\frac{1}{(2+0{\cdot}235)^2} - \frac{1}{(m+0{\cdot}77)^2}\right].$$

(*b*) $$\bar{\nu} = \mathrm{R}\left[\frac{1}{(2+0{\cdot}232)^2} - \frac{1}{(m+0{\cdot}77)^2}\right].$$

The equations (*a*) and (*b*) refer to the respective doublet components.

The Interpretation of Series Relationships.—The above-mentioned relationships between the series limits, doublet separations, &c., had been empirically discovered long before any interpretation of them could be given. The conception of stationary states of the atom and the consequent conception of spectral lines as corresponding to term differences provide a simple explanation of the series regularities.

The following interpretations refer always to emission spectra:

(1) There are two possible final states in the transitions which give the diffuse series, and these are identical with the two possible final states for the sharp series. The initial states of these transitions, on the other hand, are different for the two series. The separation of the doublet components in both series is equal to the separation of the two possible final states.

(2) There is only one possible final state in the transitions which give the principal series. Here, however, the initial states are double, and the separation of the doublets diminishes as the sequence number m increases.

(3) The first doublet of the principal series is given by transitions from the final state of the diffuse or sharp series to the final state of the principal series.

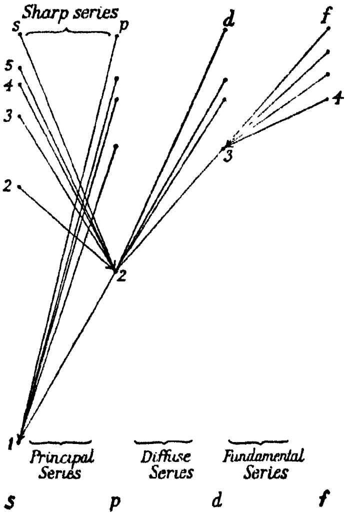

Fig. 2.—Term diagram for the arc spectrum of an alkali metal, neglecting doublet separations.

Fig. 2 illustrates these relationships in the graphical manner previously used on p. 180. The complete term diagram is given in fig. 3; this shows the fine structure of the energy levels, which gives rise to the fine structure of the lines (e.g. the doublet structure of the D line of sodium).

The magnitude of the correction constant a is arbitrary to the extent that, since n may have any integral value, an increase of a by unity is equivalent to a decrease of n by unity. For the time being we may impose the condition that $|a|$ shall be less than 0·5. This allows a to be negative. We shall subsequently learn how to fix the value of n in agreement with the demands of the atomic model and the observed chemical, X-ray, spectroscopic and other properties.

The spectral series of the alkali metals (arc spectra) may be expressed quite generally as follows:

Principal Series: $$\tilde{\nu} = \frac{R}{(1+s)^2} - \frac{R}{(m+p)^2}.$$

Diffuse Series: $$\tilde{\nu} = \frac{R}{(2+p)^2} - \frac{R}{(m+d)^2}.$$

Sharp Series: $$\tilde{\nu} = \frac{R}{(2+p)^2} - \frac{R}{(m+s)^2}.$$

Fundamental Series: $$\tilde{\nu} = \frac{R}{(3+d)^2} - \frac{R}{(m+f)^2}.$$

If we adopt Paschen's abbreviated notation, these may be written in the following forms:

Principal Series: $$\left.\begin{aligned}\bar{\nu}_1 &= 1s - mp_1\\ \bar{\nu}_2 &= 1s - mp_2\end{aligned}\right\} m = 2, 3, 4, \ldots$$

Diffuse Series: $$\left.\begin{aligned}\bar{\nu}_1 &= 2p_1 - md\\ \bar{\nu}_2 &= 2p_2 - md\end{aligned}\right\} m = 3, 4, 5, \ldots$$

Sharp Series: $$\left.\begin{aligned}\bar{\nu}_1 &= 2p_1 - ms\\ \bar{\nu}_2 &= 2p_2 - ms\end{aligned}\right\} m = 2, 3, 4, \ldots$$

Fundamental Series: $\bar{\nu}_{1,\,2} = 3d - mf; \quad m = 4, 5, 6, \ldots$.

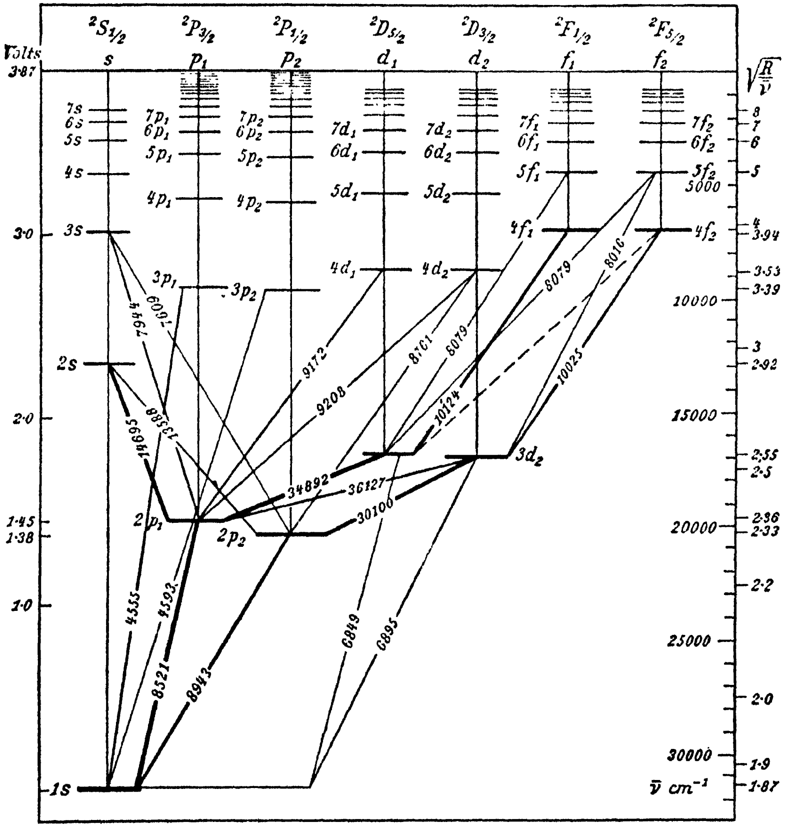

Fig. 3.—Complete term diagram for cæsium I

[From Grotrian, *Graphische Darstellung der Spektren*, Part II (Springer, Berlin).]

The subscripts 1 and 2 refer to the doublet components. For the alkali metals of higher atomic number (e.g. Cs) it is found that the *d*-terms and also the *f*-terms are double. From this it would at first sight appear that the lines of the diffuse and fundamental series ought to be quadruple. Experiment, however, shows that they are only triple. It is clear, therefore, that transitions cannot occur between *all* the possible pairs of stationary states. There must be certain so-called *selection rules*, which exclude some of the transitions. This can be seen in fig. 3, in which the observed frequencies (with the exception of the higher series numbers) are indicated by sloping connecting-lines drawn between the energy levels concerned in their emission. It is seen that all the possible combinations do not actually occur.

Note to fig. 3.—Each term has its own value of m and of a. In the figure each vertical set of terms has a constant a, but the value of a is different in the different vertical sets. For the sake of clarity the observed transitions are only indicated for the lower terms. The main lines of the spectrum are shown by heavier connecting-lines. On the right is given a scale of wave-numbers in cm.$^{-1}$, on the left an energy scale in volts, reckoned relative to the lowest level (ground state). The meaning of the symbols used in the figure and the significance of the $\sqrt{R/\bar{\nu}}$ values will become clear in due course.

As in the case of hydrogen, the energy value for the lowest level, i.e. for the ground state, must give the ionization potential of the atom. For hydrogen this corresponds to the frequency of the limit of the LYMAN series; for the alkali metals the value is given by the limit of the principal series. In the same way the potential (first resonance potential) required for excitation of the resonance line, which is the first line of the principal series, must correspond to the energy difference $1s - 2p$.

TABLE XX

	First Resonance Potentials		Ionization Potentials	
	Theor.	Exp.	Theor.	Exp.
Li	1·840 V	—	5·368 V	—
Na	2·095	2·12 V	5·116	5·12 V
K	1·610	1·55	4·321	4·32
Rb	1·582	1·6	4·158	4·16
Cs	1·448	1·48	3·878	3·88

Table XX gives a comparison between the values calculated from the spectra and those observed directly (values in electron-volts).

2. The Optical Spectra of Elements of Higher Valency

Spectra of Divalent Elements.—Even the increase of valency from one to two brings about a considerable increase of complexity in the spectra. The most important difference is that with divalent elements we have two almost completely independent term-systems, one of which has only simple levels while the other has triple levels (so-called *singlet system* and *triplet system*). In each of these systems (see fig. 4) it is possible to pick out a principal series, a diffuse series, a sharp series, and a Bergmann or fundamental series, just as for the alkali metals. There is also a series corresponding to the transitions $3d - mp$, the analogue of which for the alkali metals lies in the infra-red.

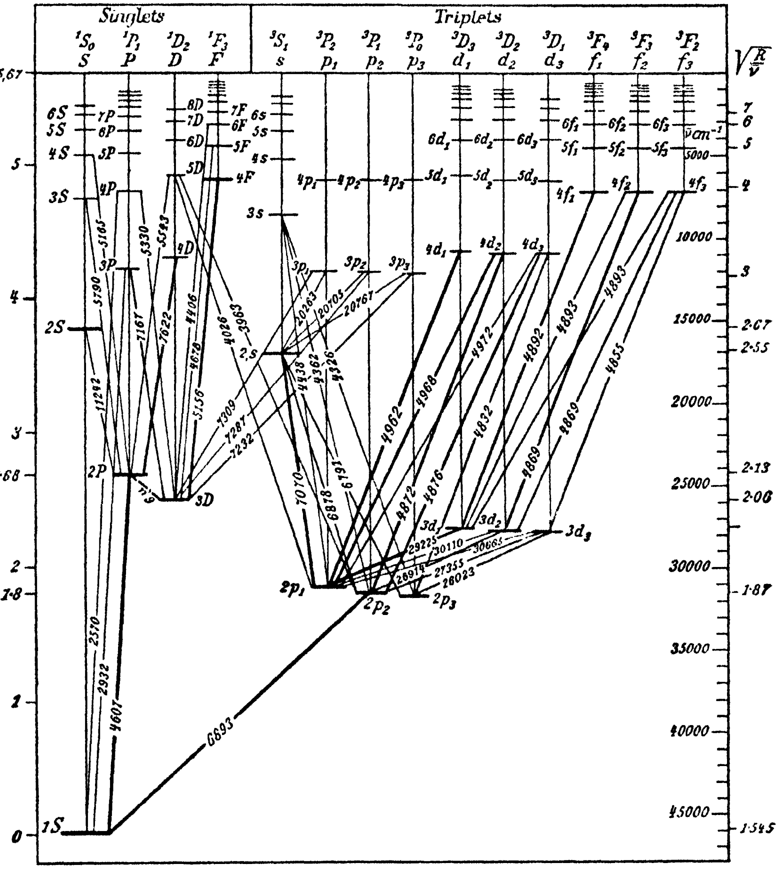

Fig. 4.—Term diagram for an alkaline earth atom (strontium I)

[From Grotrian, *Graphische Darstellung der Spektren*, Part II (Springer, Berlin).]

Term-symbols.—It follows that the terms can be denoted by the same symbols as for the alkali metals, namely, *s*, *p*, *d*, *f*. In general it is customary to designate the terms of atomic spectra by capital letters, placing a superscript 1 before the symbol to denote the singlet

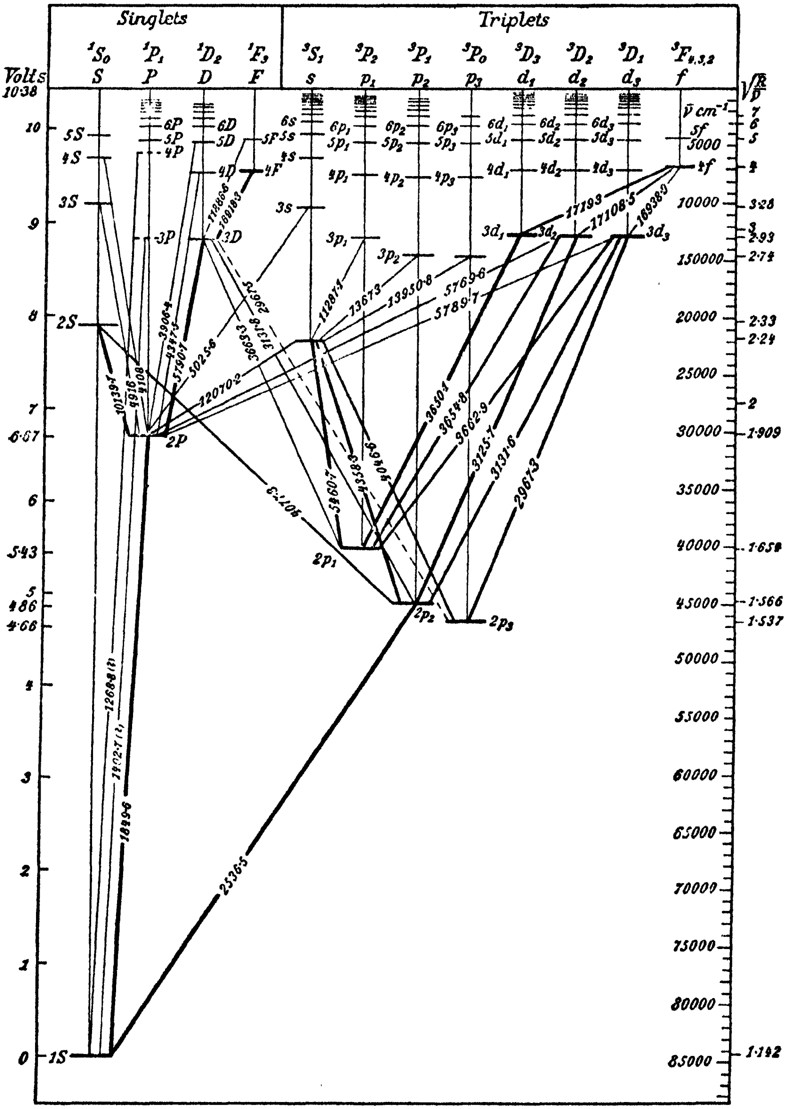

Fig. 5.—Term diagram for the neutral mercury atom

[From Grotrian, *Graphische Darstellung der Spektren*, Part II (Springer, Berlin).]

system, a superscript 3 before the symbol to denote the triplet system, and so on. Thus we have ^1S, ^1P, ^3S, ^3P, and so on. The different components of a multiple term are denoted by a corresponding subscript written after the term-symbol, e.g. $^3P_1$ (see fig. 4). For the choice of the number for this subscript see p. 321. The principal quantum number n of the term is finally placed in front of the whole symbol. For example, 4^3P_1 (which is read as "four-triplet-P-one") denotes the middle component (subscript 1) of the P-term of the triplet system for which $n = 4$. It should be noted that (as in the doublet system of the alkali metals) the S-terms of the triplet system are not triple but single, i.e. they do not share in the multiplicity of the system to which they belong. The superscript 3, however, is written in the symbol for these terms to distinguish them from the other S-terms.

Selection Rules.—In connexion with the *fine structure* of the lines, it is to be noted that the combinations of the three components of a triplet term with the three components of another triplet term do not, as might be expected, give rise to a line with the multiplicity 9. The actual line is found to have a multiplicity of at most 6. Hence there must be some restriction upon the possibilities of combination of the fine structure components of different terms, as there is upon the possibilities of intercombination between the different term systems themselves. We see (fig. 3, p. 281) that for the alkali metals there are no transitions from *s* to *d* or to *f*, that there is only one transition (of low intensity) from *d* to *s*, and none from *f* to *s*. The same is true for the divalent elements (see fig. 4). Here the transitions between the singlet and triplet systems are also seen to be relatively few. The more detailed discussion of the *selection rules* governing the possibilities of combination of terms will be given on p. 321.

As a further example we may take the term diagram for mercury (see fig. 5). Its relation to the corresponding diagram for the alkaline earth metals (fig. 4), which follows from the divalency of mercury, can be seen from the fact that we again have a singlet system and a triplet system. In addition, the lowest term is in both cases an S-term. But in consequence of the complicated structure of the mercury atom, which contains 80 extranuclear electrons, the transitions between singlet and triplet system and vice versa are quite numerous. The resonance line 2536 Å., which is used in many experiments, is a case in point (see fig. 5); so also is the pair of yellow lines 5769 and 5789 Å. The resonance line of the singlet system lies at 1849 Å. The visible triplet 5460, 4358, 4046 Å. is given by the lowest transition $^3S - {}^3P$. This gives an idea of the large separations of the components of the ^3P level (the ^3S level is simple) in comparison with the separations for lighter atoms (such as Ca or Mg).

The Helium Spectrum.—The spectrum of helium (fig. 6) is quite similar to that of an alkaline earth metal. Helium, with its two electrons surrounding a nucleus of charge two, thus exhibits a certain resemblance to an alkaline earth metal with its two valency electrons (see also p. 324). The two different states of helium (**orthohelium** and **parhelium**) have already been mentioned on p. 274. The triplet system of the helium spectrum belongs to orthohelium, the singlet system to parhelium. It can be shown that no intercombination of the two systems

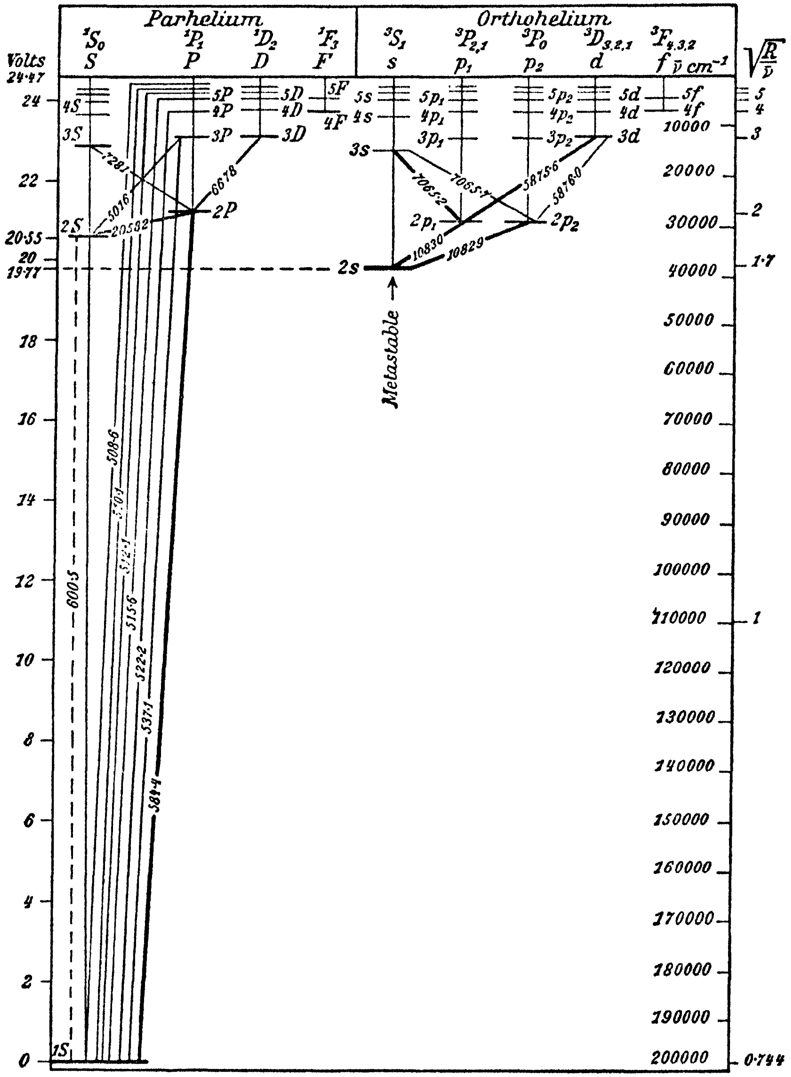

Fig. 6.—Term diagram for neutral helium

[From Grotrian, *Graphische Darstellung der Spektren*, Part II (Springer, Berlin).]

is possible. We have seen (p. 274) that there is only one proper function for the lowest state ($n = 1$). This is in agreement with observation, for the lowest term of the orthohelium system has $n = 2$. There is an energy difference of 19·77 volts between the lowest term of helium

(^1S) and the next higher (2^3S). This is the greatest known difference between a ground state and the next higher state. One consequence is that up to a velocity of about 19·8 volts electrons suffer no loss of velocity in helium gas. The other inert gases exhibit similar behaviour, though to a lesser extent. On this fact are based many technical applications of helium and the other inert gases in gas discharges.

Trivalent Elements.—As an example of a trivalent element, we may take the term diagram of aluminium given in fig. 7. In addition to the doublet terms shown there, quadruple terms (quartets) also occur for the elements of group III of the periodic table.

It can be seen from fig. 7 that the lowest term of the aluminium atom is not an S-term, as in the cases considered above, but a P-term.

Metastable States.—We have seen that there must be selection rules which preclude the possibility of certain transitions between stationary states of an atom in the emission or absorption of radiation. A very important consequence of this is the existence of excited states which cannot pass over into the ground state by emitting their excitation energy as radiation, and which cannot be produced from an atom in the ground state by the absorption of radiation. A case of this kind has already been mentioned on p. 180.

Examples of excited states of the kind in question can be found in the preceding term diagrams: in fig. 4 the 3^1D and the 2^3P_2 and 2^3P_0 levels of Sr, in fig. 5 the 2^3P_2 and 2^3P_0 levels of Hg, and in fig. 6 the 2^3S level of He. If an excited atom reaches one of these levels by emitting radiation, it cannot pass over into the ground state by further emission.

The energy of excitation of these levels can only be transferred to another atom by a collision process. Hence such excited atoms often reach a comparatively high concentration. Whereas the length of time usually spent by an atom in an excited state is of the order of magnitude of 10^{-8} second, atoms may remain in these so-called *metastable states* for periods running into seconds. The existence of such metastable states is of great importance in many photochemical reactions.

Spark Spectra.—In this chapter we have so far dealt only with the spectra of the neutral atoms of certain elements. The spectra of the singly or more highly charged positive ions (formed by the removal of one or more electrons from the neutral atom) exhibit quite analogous series relationships. The corresponding lines, however, lie much further in the ultra-violet. The reason for this lies in the increased force exerted by the nucleus upon the remaining extranuclear electrons when one or more of the latter have been removed. The relations between the spectra of neutral atoms and ions may be expected to be of the kind mentioned on p. 193 in connexion with He^+, Li^{++}, and Be^{+++}, when it was pointed out that in these cases the spectra can be derived from that of hydrogen by multiplication by the squares of the

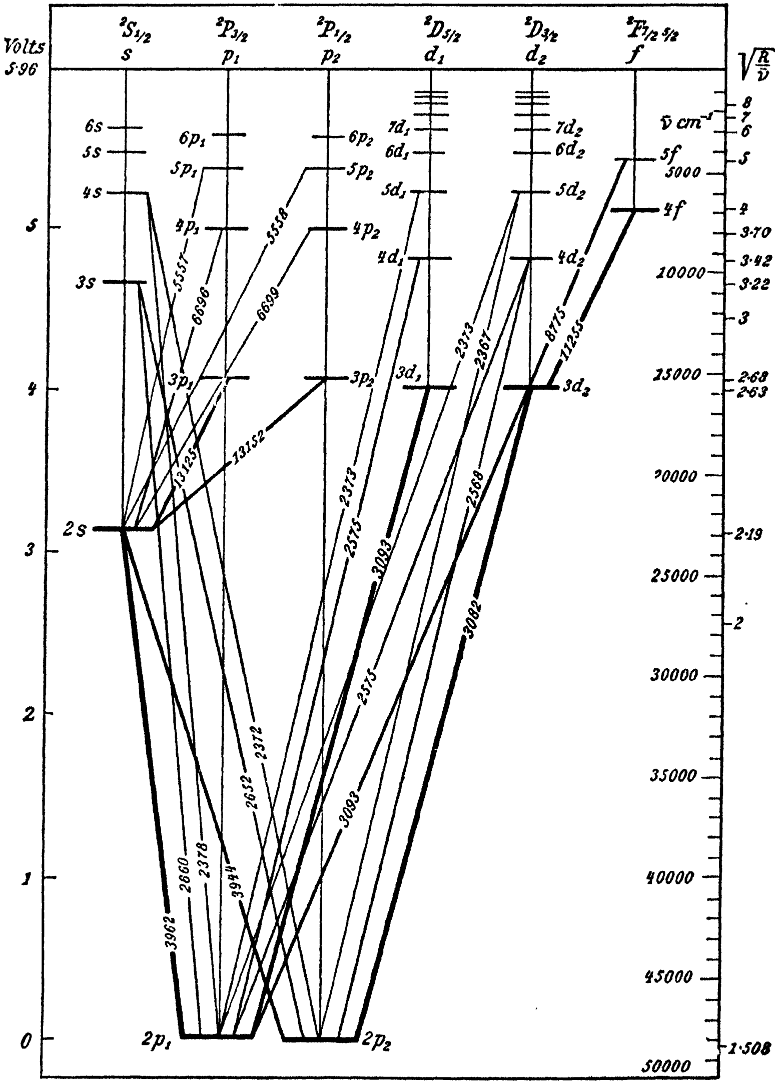

Fig. 7.—Term diagram for neutral aluminium

[From Grotrian, *Graphische Darstellung der Spektren*, Part II (Springer, Berlin).]

respective atomic numbers. For example, the H_α line of the Balmer series corresponds to a He^+ line of four times the frequency, to a Li^{++} line of nine times the frequency, and to a Be^{+++} line of sixteen times the frequency.

In applying this line of argument to the more complicated atoms, we must compare systems with different nuclear charges but with the same number of extranuclear electrons, e.g. Na, Mg^+, Al^{++}. The anticipated relationships are actually found to occur: the spectra of Na, Mg^+, and Al^{++} all have the same doublet character, although e.g. the neutral Mg atom has a singlet-triplet character. Moreover, the quantitative relationships between these three spectra is very nearly the same as for H, He^+, Li^{++}. We may take as example the series formulæ for the sharp series (considering only one component, for the sake of simplicity). We have the following:

$$\text{Na:}\quad \tilde{\nu} = R\left[\frac{1}{(3-0{\cdot}90)^2} - \frac{1}{(m-1{\cdot}38)^2}\right],$$

$$\text{Mg}^+\text{:}\quad \tilde{\nu} = 4R\left[\frac{1}{(3-0{\cdot}74)^2} - \frac{1}{(m-1{\cdot}08)^2}\right],$$

$$\text{Al}^{++}\text{:}\quad \tilde{\nu} = 9R\left[\frac{1}{(3-0{\cdot}63)^2} - \frac{1}{(m-0{\cdot}91)^2}\right].$$

The sequence number m may assume the values 4, 5, 6, ...

Thus we see that there is a marked similarity, both as regards fine structure and series formulæ, between the arc spectrum of any given element, the first spark spectrum of the element one place higher in the atomic number scale, the second spark spectrum of the element two places higher in the atomic number scale, and so on. This is known as the **spectroscopic displacement law** of SOMMERFELD and KOSSEL.

Analogies of this kind will be further traced on p. 340.

W. WIEN has devised an elegant method for deciding to which state of ionization of an atom an emitted line belongs. Use is made of a luminous canal-ray beam shot into a vacuum. The application of a transverse field causes a deflection of the charged particles, but allows the neutral atoms to pass on undeflected. Spectroscopic examination of the light emitted by the deflected and undeflected parts of the beam makes it possible to allocate the different lines either to the arc spectrum or to the various spark spectra. Special precautions are necessary to prevent charge exchanges in the beam.

Absorption Spectra.—Absorption spectra are the reverse of emission spectra, at least in the optical region at present under consideration (cf. p. 78). The absorption lines coincide exactly in wave-length with the corresponding emission lines, and in principle every emission line can also occur as an absorption line. Certain limitations are encountered, however, in connexion with experimental observation. In order that an absorption line may be observable, it is necessary that a large number of atoms shall make the corresponding transition almost simultaneously; otherwise insufficient light is absorbed from the incident beam. This means that a large number of atoms must be present in the lower of the two energy states between which the transition occurs. But the state towards which all the atoms tend to pass is the lowest energy state, the ground state. Hence under normal conditions (i.e. at low temperatures and in the absence of any special supply of energy) only those absorption lines are observed which involve transitions from the ground state. Thus hydrogen atoms do not ordinarily absorb the lines of the Balmer series, but only those of the Lyman series. In spite of the very intense lines which the mercury arc emits in the visible region, mercury vapour is quite transparent in this region: the first absorption line lies at 2536·5 Å. in the ultra-violet. As can be seen from the term diagram of fig. 5 (p. 284), the visible lines are due to transitions whose lower level is an excited state of the atom which under normal conditions does not occur in the vapour to an appreciable extent. If, however, the temperature is sufficiently high, excited atoms may occur in considerable concentration, the kinetic energy of a sufficiently large number of atoms being then high enough to excite other atoms by collision. If the excited level is not very far above the ground level, absorption lines due to transitions from the excited level may become observable at relatively low temperatures (cf. p. 180). Where higher excited levels are involved, correspondingly higher temperatures are necessary. Feeble absorption lines are observed experimentally by taking very thick layers of the absorbing substance, so as to increase the number of atoms involved. The Balmer lines of hydrogen, for example, often appear clearly in the absorption spectra of the atmospheres of stars (see fig. 8). Metastable states can also be obtained in such high concentration as to enable the absorption spectra of the metastable atoms to be observed. The absorption by excited states can also be determined indirectly by the method described on p. 157.

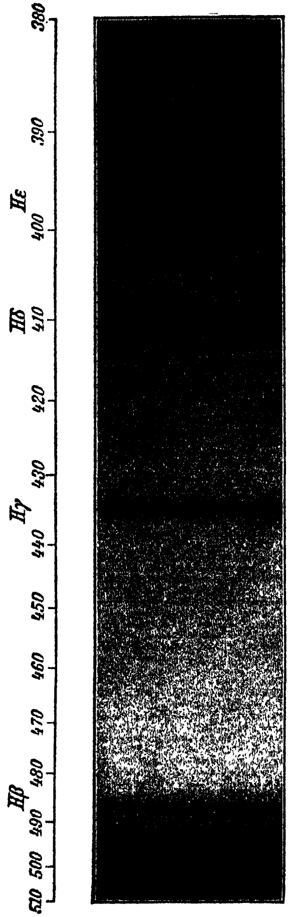

Fig. 8.—Balmer lines of hydrogen as absorption lines in a stellar spectrum (spectrum of Sirius)

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

Within any given series the intensity of absorption falls off as the sequence number increases. Yet the lines of a series can often be followed up to much higher sequence numbers in absorption than in emission.

3. X-ray Spectra

Some of the important features of X-ray spectroscopy have already been discussed in Chapter I (p. 54). In structure X-ray spectra are considerably simpler than optical spectra. We have already seen that each element of relatively high atomic number emits a number of characteristic series of X-ray lines, lying in quite widely separated spectral regions. (This is reminiscent of the hydrogen series: Lyman series in the extreme ultra-violet, Balmer series in the visible and near ultra-violet, Paschen series in the infra-red.) The X-ray series of shortest wave-length is known as the K-series, the others being called the L-, M-, N-, O-, P-series in order of increasing wave-length. An account of the present stage of our knowledge of these series has been given in Chapter I of this volume. The series become more and more complicated in the order given above, starting from the K-series.

The limits to our knowledge of this subject, evidenced by the fact that various series are unknown for certain groups of elements, depend on technical difficulties. In particular, the region lying between the short-wave ultra-violet region and the long-wave X-ray region (1000 — 50 Å.) until recently was accessible only with great difficulty to precise measurement.

These spectra are excited either by bombardment of the element in question with sufficiently fast cathode rays (see Vol. III, p. 347) or by irradiation with X-rays. In the latter method the energy quantum $h\nu$ of the X-rays used must be greater than that of the X-rays to be excited, in which case the substance irradiated gives its own characteristic spectrum, in addition to scattering the primary beam.

Fig. 65 (p. 77) gives a graphical representation of the lines of the K-series for different elements, the quantity $\sqrt{\nu/R}$ being plotted as a function of the atomic number. We see that the graph is very nearly a straight line. The corresponding analytical expression for the Kα lines is to a good approximation

$$\sqrt{\frac{\nu}{R}} = \sqrt{\frac{3}{4}}(Z-1).$$

This may be rewritten in the form

$$\frac{\nu}{R} = (Z-1)^2\left(1-\frac{1}{4}\right) = (Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right).$$

Thus we obtain a formula which is very similar to that derived for the one-electron system (see p. 183), but with the difference that the nuclear charge is diminished by approximately unity.

If the data for the Lα lines are plotted in the same way, an approximately rectilinear graph is again obtained (see fig. 12 (p. 297)). Here the approximate equation is

$$\frac{\nu}{\mathrm{R}} = (\mathrm{Z} - 7{\cdot}4)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right).$$

Thus X-ray lines can be represented as the difference of two terms. According to this view, the K-series is given by transitions to a final state of quantum number one, the L-series by transitions to a final state of quantum number two, the M-series by transitions to a final state of quantum number three, and so on.

Moreover, the individual members of the different series obey certain combination rules, discovered by KOSSEL. The following approximate relationships are found to hold between the frequencies:

$$\mathrm{K}\beta = \mathrm{K}\alpha + \mathrm{L}\alpha;\ \mathrm{K}\beta_2 = \mathrm{K}\alpha + \mathrm{L}\gamma;\ \mathrm{L}\gamma = \mathrm{L}\alpha + \mathrm{M}\alpha;\ \mathrm{K}\beta_2 = \mathrm{K}\beta_1 + \mathrm{M}\alpha.$$

These empirical relations help us considerably towards an understanding of the origin of these spectra. In this connexion absorption spectra and the energy conditions of excitation are also of great importance.

In optical spectra (see p. 289) those emission lines which are due to transitions to the ground state (or to an excited state normally present in sufficient concentration at the temperature of the experiment or to a metastable state normally represented to a sufficient extent) also appear in absorption. In the X-ray spectra now under consideration, however, this is not the case. On the contrary, the absorption spectrum (see p. 54) consists of a continuum whose intensity falls off with decreasing wave-length from a sharp long-wave edge. In the L-series three such edges are found, in the M-series five, in the N-series seven, in the O-series five, in the P-series three. In the optical case, moreover, the different members of a series can be excited successively by gradually increasing the energy of the exciting electrons (see p. 138). But for X-rays this is not so. As the energy of the exciting cathode rays is gradually increased, there is no emission of, say, the Kα lines even when the $h\nu$ value of these lines is reached. Not until the energy of the cathode rays reaches the $h\nu$ value of the absorption edge (i.e. of the series limit) does emission occur, and then *all* the lines of the K-series appear at once. The same is true for the other series. (For the complex structure of the absorption edges see p. 294.)

These phenomena indicate that all the electrons of an atom are not held by the nucleus with the same force. For if this were the case, the energy of the absorption edge (i.e. the energy required to remove an electron from the atom) would necessarily always correspond to the limit of the optical arc spectrum. Since in general only one electron is removed from an atom by X-rays, or at most a few (cf. p. 135), other ionization processes must exist besides that corresponding to the limit of the arc spectrum. The existence of different absorption edges (K, L, M, &c.)' proves further that even in the X-ray region there must be different ionization processes involving different energies.

An explanation of the mechanism of X-ray emission in agreement with the experimental observations outlined above was first put forward by Kossel in 1914. Since (as we have just seen) all the electrons in the atom are not held with equal force, we must assume that some are nearer and some farther from the nucleus. The data to be given later lead to the view that there are groups of electrons in the atom, all the members of a group being at approximately the same distance from the nucleus, i.e. situated more or less on a spherical shell surrounding the nucleus. Several such shells are supposed to be present in complicated atoms, and the maximum number of electrons to each is different for different shells. The innermost shell, in which the electrons are most strongly held on account of their proximity to the nucleus, is called the K-shell. The next is called the L-shell, and so on outwards from the nucleus (see fig. 9). In complicated atoms the inner shells are supposed to be full, i.e. to be occupied by the maximum numbers of electrons which they can hold.

Suppose now that an electron from the K-shell is ejected from the atom by means of a sufficiently energetic cathode-ray particle. The free place thus created in the K-shell may be taken e.g. by an electron from the L-shell. This results in the liberation of a quantity of energy equal to the difference between the energies of an electron in the K-shell and in the L-shell. This energy difference is emitted in the form of monochromatic radiation—the Kα line. If, alternatively, an electron drops from the M-shell into the free place in the K-shell, the larger energy quantum of the Kβ line is emitted.

The energy required to eject an electron from the L-shell is less than that required to eject an electron from the K-shell: the L-absorption edge corresponds to a longer wave-length (a smaller frequency) than the K-edge. The dropping of electrons from outer shells to a free place in the L-shell gives rise to the lines of the L-series. Analogous considerations hold for the remaining series. The atom which was ionized in the original excitation process eventually captures an electron again; this electron takes up the place which has become free in an outer shell, thereby emitting the appropriate radiation (possibly in stages).

This theory provides the first explanation of the peculiar behaviour observed in connexion with the excitation of X-ray spectra. We see that it is impossible to excite the Kα line by supplying the energy corresponding to it; for this would necessitate lifting an electron from the K-shell to the L-shell, a process which is impossible because the L-shell is already full. Analogous considerations hold also for the other lines of the K-series. In order that the emission of the K-series may become possible, an electron must be ejected from the K-shell so as to reach the outside of the atom. The energy corresponding to this ejection is therefore the minimum which will cause the K-lines to appear. We see too that, once the K-electron has been ejected, all the lines of the K-series, can occur. Thus the simultaneous appearance of all the lines of the series when a certain limit of excitation energy is exceeded, at once becomes intelligible.

The intensity relationships are also well accounted for. It is natural to assume that a free place in any given shell will most probably be filled by an electron from the next shell and that the probability of an electron falling into the free place from more distant shells decreases with the distance. Actually the Kα line is found to be the most intense (fig. 61, p. 74), and in general the intensity falls off as we pass to higher members of a series.

From the above theory we may deduce that in order to excite a series it is not necessary to eject the inner electron completely from the atom, but only to move it out to the nearest empty or incompletely filled shell. However, the energy difference between an electron when removed completely from the atom and when in a shell which is fairly remote from the nucleus is very small compared with the energy difference between an electron when in the shell just mentioned and when in the K-shell (see fig. 10, p. 295). Consequently, since the empty or incompletely filled shells are in the outer part of the atom, the energy required to remove a K-electron completely from the atom differs only slightly from that required to move the electron to an unoccupied place in an outer shell. We should expect a certain *fine structure of the absorption edges*, and this is in fact observed. The observed fine structure, however, is not altogether due to this cause.

The theory just outlined at once explains the *combination relationships* mentioned on p. 292. These can be read off without difficulty from fig. 9. A comparison may be made e.g. with the analogous combination relationships between the various members of the hydrogen series (p. 184).

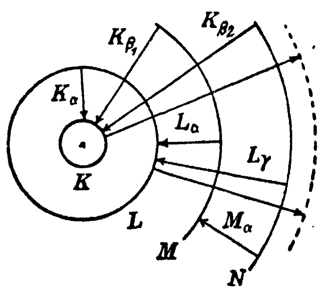

Fig. 9.—Diagram to explain the excitation of X-ray series

A comparison with the Bohr model of the hydrogen atom also gives an explanation of the significance of the *series formula* given on p. 291, which holds at least approximately for X-ray spectra. An electron in the K-shell is under the influence of the nuclear charge, but this is to some extent "screened" by the other electron in this shell. (It will be shown later that the K-shell contains only two electrons.) Hence the effect is as if the nuclear charge Z were reduced to $(Z - \sigma)$, where σ is the so-called **screening constant.** It is accordingly to be expected that the Bohr formula will hold approximately, but with the quantity $Z - \sigma$ (the so-called **effective nuclear charge** or

effective atomic number) in place of Z. The formula can only hold approximately, because no account has been taken of the effect of the L-shell. We need not discuss this further here. For the L-series the effective nuclear charge is still smaller, on account of the direct screening action of the whole K-shell and the marked additional screening action of the remaining electrons of the L-shell itself. (It will be shown later that the maximum number of L-electrons is eight.) This is in good accord with the relatively large screening constant ($\sigma = 7{\cdot}4$) which here appears in the formula (p. 292).

Term Diagrams.—Just as for the optical spectra, the stationary states (i.e. the stationary energy levels) can be represented graphically in a term diagram. In order to bring this representation into relation with the corresponding diagrams for optical spectra, the following considerations must be taken into account. The zero of the energy scale is taken as the energy of the singly-ionized atom, in the case in which the *most easily-removed electron* has been removed. The ordinary excited states of the neutral atom have lower energies than this, i.e. have negative energies. Now the energy of the atom in an excited state which gives rise to the emission of X-ray series is considerably *higher* than the zero just defined, because an electron which is ordinarily firmly held by the nucleus has been removed from the atom entirely or at least removed to the outer regions. The amount of energy required to remove such a firmly-held electron is much greater than that required to ionize the atom by removing the least firmly-held electron. Hence the *highest* energy state of the singly-ionized atom is that in which the electron removed has come from the K-shell. The state in which the electron is missing from the L-shell has a lower energy, and so on. We thus arrive at the system of energy levels represented in fig. 10. In emitting the Kα line the atom passes from the uppermost level to the next lower. This means that the free place which was previously in the K-shell has been transferred to the L-shell; or, what is the same thing, an electron has jumped out of the L-shell into the K-shell. According to the series formulæ of pp. 291, 292, we may ascribe the quantum number $n = 1$ to the K-shell, $n = 2$ to the L-shell, $n = 3$ to the M-shell, and so on. We see that the order of the levels, as compared with those of hydrogen, is inverted. As has just been pointed out, the reason for this is that the transition of an electron in the hydrogen atom is analogous to the transition of a free place or

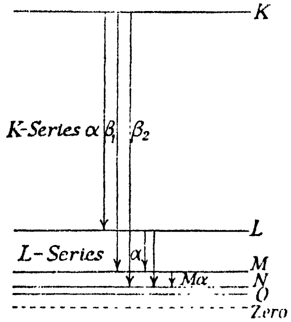

Fig. 10.—Simple term diagram for X-ray spectra

" hole " in the diagram now under consideration. Thus whereas in optical term diagrams each series has a common *final state* and various initial states, in X-ray term diagrams each series has a common *initial state* and various final states. In both cases, however, the actual *electron transitions* are from various initial states to a common final state.

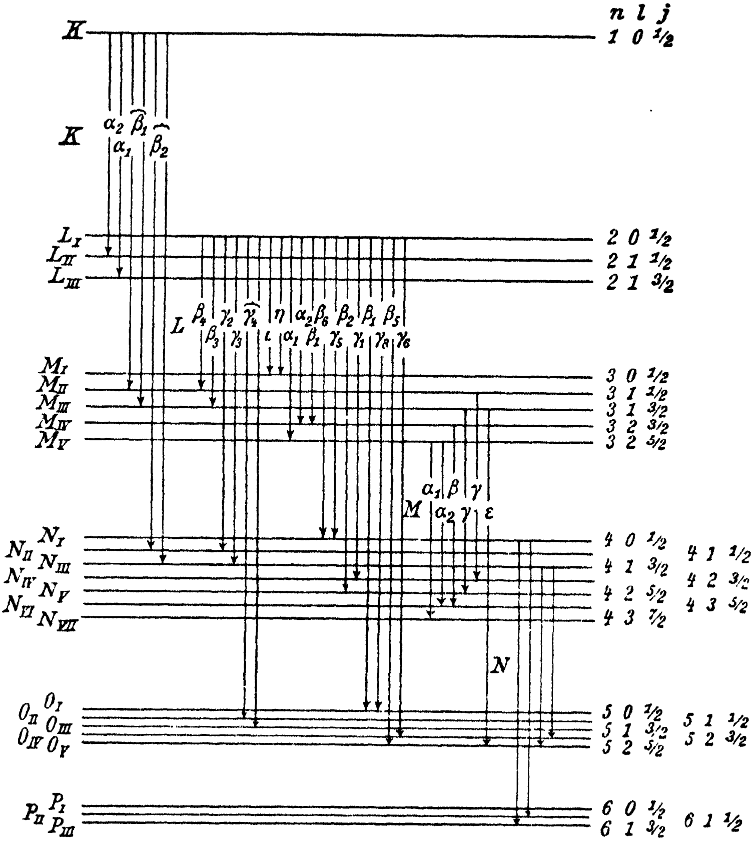

Fig. 11.—General term diagram for the X-ray spectrum of a heavy atom. The distances between the energy levels are *not* drawn to scale (see fig. 10, p. 295)

An alternative type of diagram is often used in which the K-level is placed lowest, the whole system being inverted relative to fig. 10. The transitions marked on the diagram are then actual electron transitions (not transitions of the " hole " as in fig. 10) and complete parallelism to the optical term diagrams is attained. In the light of what has been said above, however, such a mode of representation does not appear to be quite so natural, though when it is only a question of the energy differences involved the form of representation is of no consequence.

Fine Structure in X-ray Spectra.—It has already been mentioned on pp. 60 and 292 that the L-series exhibits three neighbouring absorption edges and the subsequent series even more. These L-edges are called L_{III}, L_{II}, and L_{I}, and similar symbols are used for the other series. From this we conclude that the L-shell must be triple in the sense that a free place or hole in the L-shell may be associated with three different but neighbouring energy levels of the atom.

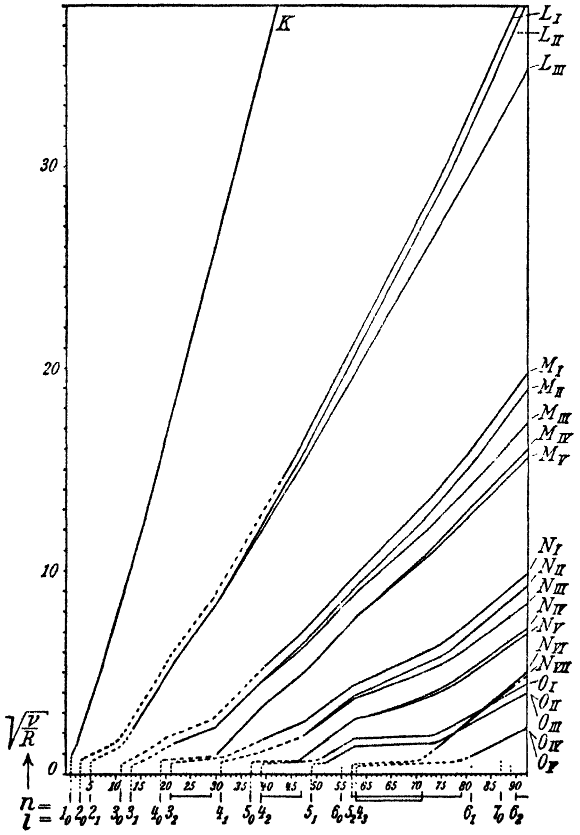

Fig. 12.—Variation of term values with atomic number

[From *Zeitschrift für Physik*, Vol. XII (1922) (Springer, Berlin).]

It has been shown by Webster and Clark and by Hoyt that the lines of the L-series are excited in successive groups as the energy of the exciting cathode rays is gradually increased. In the case of tungsten L lines first appear above 10,200 volts; but the whole series does not appear at once, as is the case for the K-series. Absorption measurements show that 10,200 volts is equivalent to the $h\nu$ value of the L_{III} edge. Only when the energy corresponding to the L_{II} edge (11,600 volts) is reached does a further group of lines appear. A third and final group makes its appearance when the cathode-ray energy reaches 12,000 volts, which corresponds to the L_I absorption edge.

By means of experiments of this kind it is possible to associate the different lines of a series with the different absorption edges and so to verify and amplify the term diagram. Fig. 11 is an improved diagram of this kind, showing the observed lines and their normal designations. The allocation of the principal quantum numbers n has already been mentioned on pp. 295 and 292. The numbers given on the right of the diagram under the headings l and j will be discussed later. We see again that all possible combinations of energy levels do not actually occur. Once more the transitions must be governed by certain selection rules (see p. 321).

The dependence of the energy levels or terms on the atomic number of the atom concerned is shown graphically in fig. 12, from which we shall be able to deduce important conclusions about atomic structure. We see that the different energy levels show different kinds of variation with atomic number. Thus L_I and L_{II} run nearly parallel; as do also M_I and M_{II}, M_{III} and M_{IV}, N_I and N_{II}, N_{III} and N_{IV}, N_V and N_{VI}, O_I and O_{II}, O_{III} and O_{IV}, and P_I and P_{II}. Each of these pairs of terms gives, in combination with some other term, a doublet with a frequency separation which is approximately inversely proportional to the principal quantum number n of the shell in question. Doublets of this kind are known as **screening doublets.** The pairs of transitions giving such doublets can be read off from fig. 11. On the other hand, the following pairs of energy levels show a different behaviour as plotted in fig. 12: L_{II} and L_{III}, M_{II} and M_{III}, and M_{IV} and M_V. These pairs give rise to doublets whose separation is proportional to $(Z - \sigma)^4$, where σ is the screening constant. As will be shown later, the energy difference between the components of these pairs of levels is connected with different orientations of the electron spin. The doublets are therefore called **spin doublets.**

B. THE SHELL STRUCTURE OF ATOMS

4. The Periodic Properties of the Elements and their Explanation

As was shown in Chapter I of this volume, the elements may be arranged in succession so that each may have ascribed to it an ordinal number (the so-called atomic number) which is the number of extra-nuclear electrons or the number of elementary positive charges upon the nucleus. In this arrangement, therefore, each element differs from the preceding one in having a nucleus with one extra positive charge and one extra electron in the surrounding electron swarm. This addition of one electron to the outer region must affect those properties of the atom (e.g. atomic volume or diameter) which depend on the extranuclear configuration. Properties of this kind have been considered in connexion with figs. 1 and 2 (pp. 7 and 8), when it is found that the variation with atomic number is not always in the same direction, but is *periodic*. This is true e.g. of the atomic volume (see fig. 1, p. 7) and is particularly true of the chemical properties (see the periodic table, Table I, p. 4). The spectral properties of atoms show a similar periodicity. Thus, as we have seen on p. 277, all the alkali metals have similar spectra. The periodicity of spectral character is particularly noticeable in the case of the term multiplicity. Here we have the so-called **alternation law** of RYDBERG, which states that neutral elements of odd atomic number have terms of even multiplicity, while neutral elements of even atomic number have terms of odd multiplicity. It is to be noted that the multiplicity here referred to is the *term* multiplicity, not that of groups of spectrum lines. Table XXI shows the alternation law for the fourth period of the periodic table (atomic numbers 19 to 26).

TABLE XXI.—TERM MULTIPLICITIES

19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe
	singlet		(singlet)				
doublet		doublet					
	triplet		triplet				triplet
		quartet		quartet		quartet	
			quintet		quintet		quintet
				sextet		sextet	
					septet		septet
						octet	

The periodicity of the properties depending on the arrangement of the extranuclear electrons indicates that, in the building up of heavier atoms by successive increase in the nuclear charge and increase in the number of extranuclear electrons, there must be a periodic recurrence of similar electronic configurations. This is reminiscent of the shell-like structure of atoms already referred to in connexion with X-ray spectra (p. 293). We shall now go into this question in rather more detail.

The electronic configurations of the inert gases all show a remarkable stability. The numbers of electrons involved are: He, 2; Ne, 10; A, 18; Kr, 36; Xe, 54; Rd, 86. The great stability is manifested firstly in the extreme chemical inertness of the inert gases and secondly in the tendency of elements of neighbouring atomic numbers to assume the inert-gas structure. We have already mentioned that the elements which follow the inert gases in the periodic table have an electropositive character, i.e. are able to lose electrons relatively easily, the number lost being just sufficient to reduce the extra-nuclear configuration to that of the preceding inert gas. On the other hand, those elements which precede the inert gases have a strong electronegative character, being readily able to take up the number of electrons required to make up the inert-gas structure. In view of these facts, we shall not go far wrong in assuming that each inert gas represents the completion of a shell. In the alkali metal immediately following an inert gas the extra electron becomes the member of a new outer shell. This is in agreement with the large increase of atomic volume occasioned by the introduction of this new electron (see the peaks in the atomic diameter graph of fig. 1, p. 7). The introduction of a further electron to give an alkaline-earth atom clearly adds a second member to the shell previously begun; for the atomic volume, instead of increasing, becomes less (as is to be expected on account of the simultaneous increase of nuclear charge). Thus, for example, the radius of the hydrogen atom in the ground state is 0·532 Å., while that of He^+ is only half this figure. In the neutral helium atom the screening effect of the electrons makes the radius greater (actually 0·3 Å.), but not nearly so great as for hydrogen.

It is possible to obtain more direct evidence for the assumption that the extra electrons of the atoms following an inert gas occupy a new shell in the structure. Let us consider the ionization potentials, i.e. the amounts of work (expressed in electron-volts) required to remove an electron from the neutral atom (or from the singly, doubly, &c., ionized atoms respectively) in the ground state. These potentials are collected in Table XXII for a number of elements, so far as they are at present known. Some of the numbers are derived from spectroscopic data (i.e. from the limits of the principal series, see p. 280). We consider first the amounts of work required to remove the *first* electron. We see that the values increase with increasing atomic number until an inert gas is reached. Then there is a sudden drop: the next electron (in the succeeding alkali metal) is held very much more loosely than the electrons of the preceding inert gas, although the nuclear charge is greater for the alkali metal. This is simply a quantitative expression of the ease with which the alkali metals can form positive ions. The same sort of thing is found when we consider the work required to remove the *successive* electrons from one and the same element. Thus in the case of potassium the removal of the nineteenth electron (i.e. the one in excess of the number for an inert gas) requires only about an eighth of the energy subsequently necessary to remove the eighteenth electron (see Table XXII). Of course the attraction of the nucleus is enhanced by the removal of the nineteenth electron; but this cannot account entirely for the much larger amount of work required to remove the next electron. For consider the case

TABLE XXII.—WORK REQUIRED TO REMOVE SUCCESSIVE ELECTRONS (IN ELECTRON-VOLTS) *

Atomic Number	Element	Work required to remove the *n*th Electron					
		1	2	3	4	5	6
1	H	13·54					
2	He	24·45	54·12				
3	Li	5·37	(75·8)	122			
4	Be	9·50	18·14	(154)	216·50		
5	B	8·34	24·20	37·79	(261·0)		
6	C	11·20	24·30	46·30	64·23	(395)	
7	N	14·49	29·56	47·20	(73·50)	97·4	
8	O	13·56	35·00	54·88	77·0	110·8	137·4
9	F	18·60	32·30	(62·50)	86·6	102·3	
10	Ne	21·48	41·00				
11	Na	5·12	47·0				
12	Mg	7·61	14·97	80·0			
13	Al	5·95	18·75	28·30	122·0		
14	Si	7·39	16·25	33·35	44·95	169	
15	P	10·30	19·80	30·0	48·0	64·80	
16	S	10·31	23·30	32·1	47·1	69·0	88·0
17	Cl	13·10	24·60	39·6	47·4	67·6	88·7
18	A	15·70	27·82				
19	K	4·32	31·70				
20	Ca	6·08	11·82	51·0			
21	Sc	6·70	12·80	24·6	(72·2)		
22	Ti	6·81	13·60	(28·0)	43·06	(95·70)	
23	V	6·76	14·70	29·6	48·30	64·90	122
24	Cr	6·74	16·60		50·40	72·80	
25	Mn	7·40	15·70			75·70	
26	Fe	7·83	(16·50)				
27	Co	7·81	17·20				
28	Ni	7·64	18·20				
29	Cu	7·69	20·50				
30	Zn	9·35	17·89				
31	Ga	5·97	18·90	30·6			
32	Ge	(9·5)	16·00	32·0	45·30		

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* The figures for the 2nd, 3rd, . . . electrons refer to the removal of the electron in question after the preceding electrons have been removed. Thus e.g. the total work required to remove four electrons from the carbon atom is 11·2 + 24·3 + 46·3 + 64·2 = 146 electron-volts.

TABLE XXII—(*continued*)

Atomic Number	Element	Work required to remove the *n*th Electron					
		1	2	3	4	5	6
33	As	(11·5)		(28·0)		62·4	
34	Se	(9·5)					81·40
35	Br	(11·60)					
36	Kr	13·90	26·4				
37	Rb	4·16					
38	Sr	5·67	11·0				
39	Y	6·50	12·30	20·60			
40	Zr				34·20		
45	Rh	7·70					
46	Pd	9·0					
47	Ag	7·54	21·0				
48	Cd	8·95	16·8				
49	In	5·76	16·8	27·91			
50	Sn	7·36	14·53	30·49	40·57		
51	Sb	(8·50)			43·91	55·40	
54	Xe	12·0	(24·25)				
55	Cs	3·88					
56	Ba	5·19	9·95				
57	La	5·50	(12·50)				
58	Ce	6·91					
59	Pr	5·76					
60	Nd	6·31					
62	Sm	6·55					
65	Tb	6·74					
66	Dy	6·82					
70	Yb	7·06					
79	Au	9·25					
80	Hg	10·39	18·67				
81	Tl	6·08	(21·0)	30·6			
82	Pb	7·39	14·98	31·93	43·90		
83	Bi	8·00		25·90			
88	Ra		10·2				

of the next element calcium. Here the amount of work necessary to remove the twenty-first electron is rather less (6·08) than that required subsequently to remove the next electron (11·82). This is due to the reduction of the screening. The two amounts are nevertheless of the same order of magnitude. In order to remove one *more* electron from calcium, a very much greater amount of work (51·0) is found to be necessary—evidently because a new shell has to be broken into. The same sort of thing is exhibited in the case of the next element scandium. Here three electrons can be removed relatively easily, but the fourth suddenly requires a much greater expenditure of work (see Table XXII). If we make due allowance for the reduction of screening, the above considerations show quantitatively the great stability of the electron configurations of the inert gases and the beginning of new shells in the alkali metals.

The distributions of charge density, as calculated by wave mechanics, likewise show maxima at different distances from the nucleus, corresponding to the successive shells at present under discussion (see fig. 13).

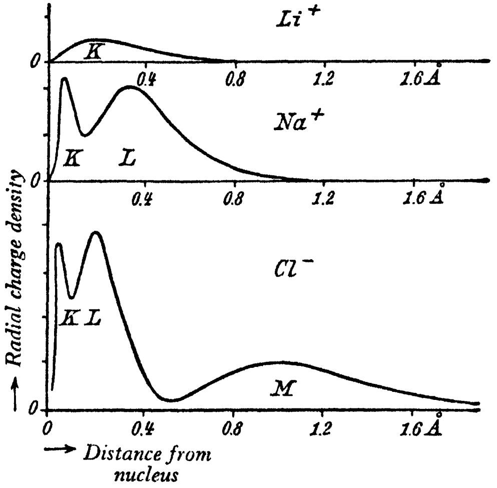

Fig. 13.—Radial distribution of charge density for Li^+, Na^+, and Cl^- (after Pauling)

Making use of the periodic table and the table of ionization potentials given above, we might now attempt to deduce the numbers of electrons contained in the different shells for different elements. In this connexion, however, we have to take account of the following consideration, which throws some doubt on the solution of the problem in this simple form. The configurations in the neighbourhood of the inert gases may be regarded as unique: the completion of shells at the inert gases and the commencement of new shells at the alkali metals may be taken as certain. The sub-groups and the transitional groups, however, cannot be brought into the scheme without further investigation. It is quite possible, for instance, that when the M-shell has been built up to a certain (incomplete) extent, the next electrons may enter the N-shell, i.e. that new shells may be commenced before the preceding shells are completed. This will obviously be a question of the energy relationships involved in the process of building up successive atoms of the periodic table by successive increases of the nuclear charge and additions of extra-nuclear electrons. The configuration which results will be that which has the lowest energy in each case. As we shall see later, considerations of optical spectra give a clear answer to questions of this kind.

X-ray spectra also give information on this point, as can be seen in the following way. In the first place, the complete linearity of the X-ray spectra of the K-series and the approximate linearity of the L-series are in striking contrast to the marked periodicity of other properties of the elements when arranged in order of atomic number. It is not difficult, however, to understand how this must come about, in the light of what has been said above. The innermost shells of electrons are responsible for the production of the X-ray series mentioned. The electrons in these shells are strongly influenced by the nuclear charge, but this influence is to some extent screened by the presence of the remaining extra-nuclear electrons of the atom. Regarding the different shells as occupying fixed positions in space around the nucleus (cf. fig. 44, p. 271, and fig. 9, p. 294), we may resolve this screening effect into three parts: (1) that due to the electrons of shells *nearer the nucleus* than the shell of which the selected electron forms a part, (2) that due to the electrons in shells *farther from the nucleus*, and (3) that due to electrons in the *same* shell as the selected electron. To a first approximation we may regard the screening of part (1) as complete, i.e. we may suppose the nuclear charge to be reduced by a number of elementary units equal to the number of electrons in the inner shells concerned. The second part of the screening can be computed by assuming the outer shells to be spherically-symmetrical charge distributions upon spheres with the radii of the respective shells. The potential energy of an electron within such a spherical shell of radius ρa_0 (where a_0 is the radius of the first Bohr circular orbit) and of total charge Ze is $Ze^2/(\rho a_0)$. This decreases as ρ increases. Thus it is easy to see, for example, that the addition of an electron to the N-shell has only a vanishingly small effect on the energy of an electron in the K-shell in comparison with the simultaneous increase by unity of the nuclear charge. The third part of the screening effect, namely that due to the electrons in the same shell as the selected electron, is difficult to estimate; but at any rate the screening due to each such electron is only partial.

By following the train of thought first suggested by Bohr, i.e. by regarding each element as built up from the preceding element by the addition of one extra-nuclear electron and the simultaneous increase of the nuclear charge by unity, it is thus possible to draw some conclusions as to the position taken up by the new electron from consideration of the screening to which it is subjected. X-ray spectra give us quantitative information about this screening. In fig. 14 (which corresponds to a portion of fig. 12, p. 297, on a larger scale) the ordinates of the graphs are the square roots of the term values. These are proportional to the **effective nuclear charge** ($Z - \sigma$), where σ is the screening constant (see p. 294). Hence σ may be calculated directly. A linear slope of the graphs indicates that σ is constant, i.e. that the newly-added electrons are being incorporated in shells lying far outside the shell concerned in the X-ray term. Where the slope of the graphs becomes flatter, the value of σ must increase. This indicates the beginning of a stronger screening action, i.e. the incorporation of the new electron in a shell nearer the shell under consideration. Where a graph runs horizontally, the effect of unit increase of Z must be completely compensated by the screening effect of the newly-added electron (i.e. $Z - \sigma =$ constant), which means that this electron must take up a

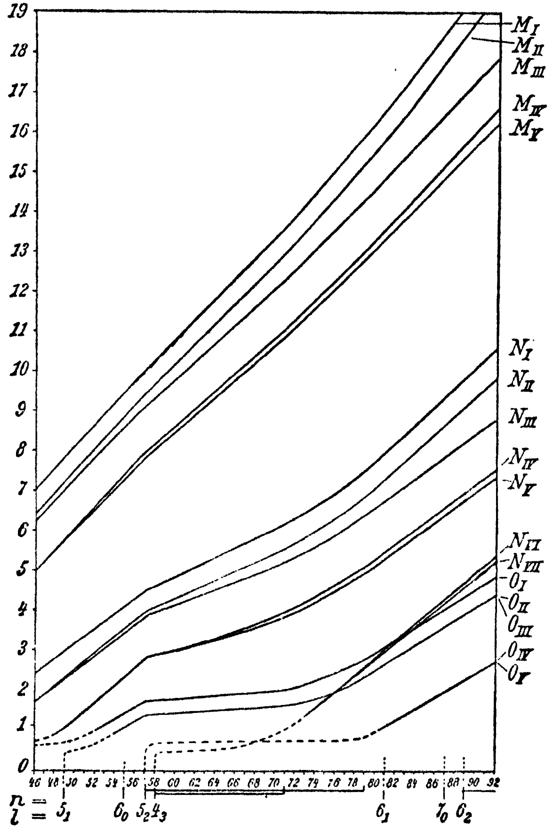

Fig. 14.—Variation of X-ray term values with atomic number (enlargement of part of fig. 12, p. 297)

place in a shell which is *nearer* the nucleus than the shell under consideration. Inspection of the shapes of the graphs shows clearly that discontinuities occur at the boundaries of the groups of elements 21–28, 39–46, and 58–72. Whereas in the remaining elements the electrons added in the building process take up positions in an outer shell, in the elements of these groups the added electrons clearly go into an inner shell. These latter elements are precisely those which are known to show variable valency and variable chemical relationships. From the magnitude of the change of slope of the individual graphs it is possible to deduce which shell the newly-added electrons enter. For the group 21–28 it is the M-shell, for the group 39–46 the N-shell, and for 58–72 the N-shell again (not the O-shell, as is proved by the horizontal course of the O graphs, see fig. 14).

The quantitative calculation of the number of electrons in the different shells from the screening constants presents great difficulties. It must be remembered that, in terms of the Bohr model, the " outer " electron orbits may have a large eccentricity and may therefore penetrate into the region of the inner shells. The exact calculation of the effect of this penetration is very difficult, though the above qualitative conclusions remain unaffected. There is, however, another method by which the problem may be treated. This method, which was also put forward by Bohr, will be considered later (see p. 334).

C. The Vector Model of the Atom

5. The Atomic Structure of Hydrogen-like Elements

Resemblance of the Alkali Metals to Hydrogen.—As has been mentioned on p. 210, the Bohr atomic model is not capable of providing a satisfactory solution of the problem of the helium atom (nucleus and two electrons), for which it is necessary to make use of wave mechanics (see p. 273). It would therefore seem at first sight hopeless to try and derive the behaviour of still more complicated atoms from the Bohr model. However, a knowledge of the periodicity of the chemical properties, and the spectral and other physical properties of the elements, provides a means for overcoming the difficulties, at least in part. Let us consider the alkali metals. According to what has been said above, one of the electrons in an alkali metal atom occupies a peculiar position, in that it moves in the outer parts of the atom, whereas all the remaining electrons are confined to completed shells lying more or less near the nucleus. Hence it is permissible to make a rough model of the atom by supposing the single outer electron to circulate around an atomic " core " * whose dimensions are small relative to the dimensions of the outer orbit. The outer electron is generally referred to as the **valency**

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* Ger. *Atomrumpf.*

electron, since it is the one which takes part in chemical combination. The nuclear attraction on the valency electron is strongly screened by the electrons of the core. We see that this model is very similar to the Bohr model of the hydrogen atom, and we may expect to be able to deduce (as for hydrogen) those properties of the alkali metal atom which depend on the special part played by the valency electron.

These considerations also find support from the wave-mechanical treatment of the problem. Unsöld has shown that when all the shells are complete the wave-function involves only spherical functions depending on the radius r. Thus there are no nodal planes or nodal cones and the charge distribution is spherically symmetrical, as in the cases with $l = 0$ treated on p. 268. Now according to our model the singly-charged ions of the alkali metals have only completed shells, having lost the outer valency electron. The actual charge distribution for Li^+ and Na^+ have been shown in fig. 13 (p. 303). The corresponding distribution for K^+ is approximately that given for Cl^- in the same figure The intensity of reflection of X-rays from alkali halide crystals depends on the charge distribution in the atoms. It has been found that the intensities calculated from the charge distributions of fig. 13 are in good accord with observation. Wave-mechanical calculations give the following values for the effective radius of the outermost spherical "electron cloud", i.e. the radius of the "core" in the rough model referred to above: Li^+, 0·28 Å.; Na^+, 0·41 Å.; K^+, 0·82 Å.; Rb^+, 1·20 Å.; Cs^+, 1·48 Å. On the other hand, the atomic radii of the *neutral* alkali metal atoms, as deduced from gas-kinetic theory and from melting-points and similar data, are: Na, 1·62 Å.; K, 1·91 Å. This is therefore the radius of the "orbit" of the valency electron. We see that there is a certain resemblance to the hydrogen atom and that the representation of an alkali metal atom as a one-electron system is quite well justified.

The Vector Model.—A certain difficulty is encountered when an attempt is made to develop the ideas just outlined. We have seen that the Bohr model has shortcomings, and we therefore cannot rely on conclusions drawn from models of Bohr type. In order to get completely accurate results it is necessary to apply the wave-mechanical method. Unfortunately it is quite impossible to form any mental picture of the wave-mechanical model of a complicated system, because it has not been found possible to construct any representation of the wave functions in ordinary three-dimensional space. Even if such a representation were possible, it would be so complicated that it would be very difficult to work with. Hence it is found advantageous to make use of a simplified model, just as the chemist uses formulæ which are symbols for much more complicated systems. The chemist writes his formulæ in one plane; and hence in order to take account of the three-dimensional relationships which hold in chemical compounds it is necessary to ascribe to certain configurations properties which do not follow from the plane symbols alone. Even a three-dimensional chemical formula with its spatially-directed valency bonds is only a greatly simplified symbol for what is probably in reality a very complicated system of electric and magnetic fields. The same sort of symbolic representation is adopted in atomic physics. The ideas of definite orbits and point-electrons are taken over from the BOHR theory, but the properties ascribed to the angular momentum vectors associated with these orbits and electrons are those deduced from wave mechanics. In this way we obtain a convenient and nevertheless exact representation which, though only in the nature of a symbol adopted so as to avoid the actual difficulties and complexities of the system, is of great practical use. That the symbol must not be taken too literally is clear, for example, from the fact that all the ellipses of maximum eccentricity ($l = 0$, see p. 198) have no orbital angular momentum.

As we shall see, the atomic model under discussion is chiefly concerned with the vectors associated with the different quantum numbers. We shall therefore refer to it as the **vector model.**

Alkali-like Systems.—We shall now develop the model for alkali-like systems, i.e. those which can be regarded as consisting of a core and a single outer or valency electron. To this class belong Mg^+, Al^{++}, &c., besides the alkali metal atoms themselves. We must bear in mind the differences to be expected in such systems as compared with the hydrogen atom. The principal difference is that the core cannot be regarded as a point-charge like the hydrogen nucleus. The outer electron moving in its orbit (or the corresponding charge distribution in its pulsation) may be expected to cause a polarization of the core, i.e. a displacement of the charges within it. As a consequence of this, the force exerted by the core upon the electron at the different points of its orbit will not be expected to be the same as if the core were a point-charge. The effect will be similar to that which results from the variability of the mass of the electron in the hydrogen atom: the perihelion of the orbit will precess, and the electron will trace out a rosette of the type illustrated in fig. 57, p. 201. In the present case, however, the effect is much stronger than that due to the variability of mass in the hydrogen atom. The angle through which the perihelion turns in one revolution of the electron in its orbit is much greater here. In orbits of large eccentricity and therefore small perihelion distance (or, in the wave-mechanical model, models of vibration for which l is small and maxima of charge density occur at small distances from the nucleus) it is to be expected that the electron will actually penetrate into the core (or, in the wave-mechanical model, that the inner maxima of charge density will interact strongly with the charge distribution of the inner " shells "). For the sake of simplicity the BOHR model will be referred to exclusively in what follows. The reader may be left to translate the description into terms of the wave-mechanical model in the manner indicated above, in so far as this can be done simply.

It is to be expected that an electron in a *penetrating orbit*, such as is represented in fig. 15, will interact very strongly with the core of the atom. The effective nuclear charge will be greater for such an orbit, i.e. the screening will be less, than for a non-penetrating orbit. This indicates that the fine structure, which in the hydrogen spectrum is due only to mass variability or applied field, must be much more marked in the alkali-like spectra. This may be expressed in terms of our model by saying that the elliptical orbits of different eccentricity, which in the hydrogen atom are energetically very nearly equivalent, are energetically very different in the alkali-like atom. The question arises whether we can ascribe the *s*-, *p*-, or *d*-states to definite orbits. Obviously the above considerations on the relation between orbit shape and energy will be of importance in this connexion.

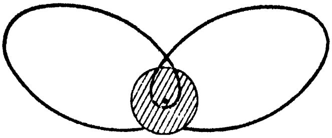

Fig. 15.—Penetrating orbit with marked precession of the perihelion.

Effective Quantum Number and Quantum Defect.—It was shown on p. 277 that the alkali spectra can be represented by means of terms of the form $R/(n+a)^2$. It is not possible to deduce the value of n from experimental data, but only the value of $(n+a)=\bar{n}$ (the so-called **effective quantum number**). Hence the allocation of numerical values to n and a separately was considered to be arbitrary and a certain convention was adopted for the sake of convenience (see p. 280.) In the light of our atomic model, however, we can make a definite statement about the value of n. Using the value of n derived from the atomic model, we shall express the effective quantum number by the equation $\bar{n}=n-q$, where q is the so-called **quantum defect.**

We know from X-ray spectra that the successive shells are associated with the successive principal quantum numbers n in the way outlined on p. 295; i.e. for the K-shell, $n=1$; for the L-shell, $n=2$; for the M-shell, $n=3$; &c. Accordingly the valency electron of Li must, in the ground state, occupy an orbit with $n=2$, since the shell with $n=1$ is already filled up with two electrons. Similarly, the valency electron of Na must, in the ground state, occupy an orbit with $n=3$, since the shell begun at Li is already completed at Ne. In the same way, the valency electron of K must occupy an orbit with $n=4$, that of Rb an orbit with $n=5$, and that of Cs an orbit with $n=6$.

Now provided that the orbit in which the electron moves is far outside the atomic core, the nuclear charge Z will be so screened by the $(Z-1)$ electrons of the core that it is effectively reduced to unity (see p. 304). Thus for such non-penetrating orbits the energy will be quite similar to that for the hydrogen atom, for the electron is under the influence of a nucleus of unit effective charge. The spectral term in question will have practically the same value as the corresponding hydrogen term, viz. R/n^2. Here the quantum defect q is practically zero. On the other hand, orbits which approach or actually penetrate into the core will differ markedly from hydrogen orbits; they will have an effective quantum number $\bar{n}$ which is less than n, i.e. the quantum defect will be appreciable. That $\bar{n}$ must be *smaller*, and not larger, than n is clear from the fact that the influence of the nucleus on the electron over a portion of its orbit is *greater* than would correspond to unit nuclear charge, so that the orbit will resemble a hydrogen orbit of *lower* quantum number. The quantum defect q in the equation $\bar{n} = n - q$ will therefore be a positive quantity and the name " defect " is justified.

Table XXIII gives the values of the effective quantum numbers and quantum defects for the different alkali metals, as derived from

TABLE XXIII.—EFFECTIVE QUANTUM NUMBERS $\bar{n}$ AND QUANTUM DEFECTS q

		$n = 2$		$n = 3$		$n = 4$		$n = 5$		$n = 6$	
		$\bar{n}$	q	$\bar{n}$	q	$\bar{n}$	q	n	q	$\bar{n}$	q
Li	*s*	1·60	0·40	2·60	0·40	3·60	0·40	4·60	0·40	5·60	0·40
	p	1·97	0·03	2·96	0·04	3·95	0·05	4·95	0·05	5·95	0·05
	d			3·00	0·00	4·00	0·00	5·00	0·00	6·00	0·00
	f					4·00	0·00	5·00	0·00	6·00	0·00
Na	*s*			1·63	1·37	2·64	1·36	3·65	1·35	4·65	1·35
	p			2·12	0·88	3·13	0·87	4·14	0·86	5·14	0·86
	d			2·99	0·01	3·99	0·01	4·99	0·01	5·99	0·01
	f					4·00	0·00	5·00	0·00	6·00	0·00
K	*s*					1·77	2·23	2·80	2·20	3·80	2·20
	p					2·23	1·77	3·26	1·74	4·27	1·73
	d					3·79	0·21	4·77	0·23	5·75	0·25
	f					4·00	0·00	5·00	0·00	6·00	0·00
Rb	*s*							1·87	3·13	2·87	3·13
	p							2·34	2·66	3·35	2·65
	d							3·66	1·34	4·66	1·34
	f							4·99	0·01	5·99	0·01
Cs	*s*									1·94	4·06
	p									2·41	3·59
	d									3·54	2·46
	f									5·98	0·02

the series relationships (cf. p. 279 for potassium). From the table it can be seen that the orbits which are nearest to hydrogen orbits (i.e. have the smallest q-values) are those corresponding to the f-terms. Then follow in order those corresponding to the d-, p-, and s-terms. This will therefore be the order of increasing eccentricity, for it is the orbits of greatest eccentricity which penetrate to the greatest extent into the atomic core. Bearing in mind the relationship between eccentricity and the quantum number l (see fig. 55, p. 200), we therefore arrive at the following allocation of l-values to the different terms:

Term	*s*	*p*	*d*	*f*	*g*
l	0	1	2	3	4

The same conclusions may be arrived at by considering the term diagram (e.g. for Cs, fig. 3, p. 281). On the extreme right of the figure referred to are plotted the values of $\sqrt{R/\nu}$, i.e. of the effective quantum numbers, so that the deviation from the hydrogen value can be read

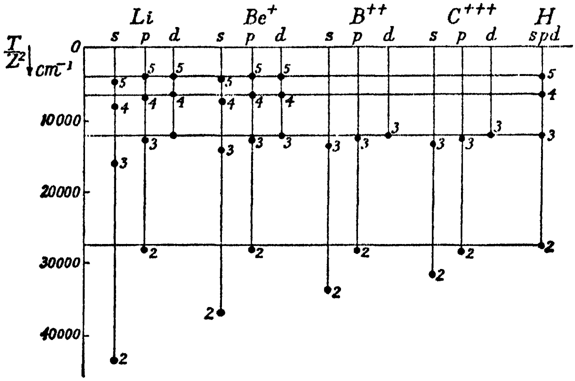

Fig. 16.—Terms of lithium-like electronic systems

off directly for each term. The terms themselves are marked (on the left) with symbols in which the first number is the principal quantum number as derived from the atomic model. Since l cannot be greater than $n - 1$, it follows (and can be seen from the term diagram) that the d-terms first appear when n becomes equal to 3, the f-terms when n becomes equal to 4, and so on.

The spectra of other alkali-like systems also furnish evidence of the relevance of the discussion. Fig. 16 shows the term-values for those spark spectra of Be, B, and C which involve the same electronic configuration as neutral Li. Since in these spark spectra the frequencies of the lines (and also the values of the terms) are proportional to Z^2, it is convenient, as in the figure, to compare the values of T/Z^2 instead of the term-values T. The values for hydrogen are shown on the right for purposes of comparison. The numbers beside the points are the respective values of n.

6. The Fine Structure of the Alkali-like Spectra

The Effect of Electron Spin.—The considerations outlined above enable us to understand the various sets of terms (s, p, d, &c.) occurring in the case of the alkali metals. The spectra of these metals show a greater complexity, however, in that all the terms (with the exception of the s-terms) are double. An explanation of this has been sought in terms of the spin of the electron (UHLENBECK and GOUDSMIT, 1925), in virtue of which the electron must be regarded as having both a mechanical angular momentum and a magnetic moment of its own (see p. 209).

To what extent can the spin of the electron affect the energy level of an atom? We shall first consider a system with only one electron. In the BOHR model, the general features of which we have adopted in our symbolization of the atom, the electron is supposed to be circulating in an orbit round the nucleus. This orbital motion is associated with a certain angular momentum, the value of which is measured by the quantum number l of p. 267 (more accurately, by $\sqrt{l(l+1)}$; compare the rotator, p. 265), the unit of angular momentum being $h/(2\pi)$. This angular momentum may be represented by a vector $\boldsymbol{l}$ whose magnitude is an integral number of the fundamental units and whose direction is as indicated in fig. 58, p. 203, i.e. normal to the plane of the orbit in which the electron circulates. In what follows we shall refer to $\boldsymbol{l}$ as the **orbital angular momentum vector.** Now on account of its spin the electron has an angular momentum of its own, the magnitude of which is $\frac{1}{2}h/(2\pi)$. We may also represent this by the so-called **spin vector** $\boldsymbol{s}$. The corresponding quantum number is here $\frac{1}{2}$ and is denoted * by s. This spin vector combines vectorially with the orbital angular momentum vector, giving the **total angular momentum vector** $\boldsymbol{j}$ in accordance with the vector equation

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}.$$

We may expect that the quantum number j measuring the total angular momentum, like other quantum numbers, will only be able to change by integral amounts. As we shall see below, this expectation is justified by the facts.

The coupling of the orbital and spin motions of the electron may be thought of as follows. We know that a circulating electric charge is associated with a magnetic field in the direction of the axis of rotation. Thus the orbital circulation of the electron produces a magnetic field in the direction of the orbital axis (normal to the plane of the orbit), and similarly the spin of the electron about its own axis produces a magnetic field in the direction of this spin axis. Now we have seen on p. 204 that a magnetic field influences a circulating charge in such a way as to cause the axis of circulation to precess about the field direction. Hence we must regard the orbital electron as spinning on its own axis, while at the same time the spin axis precesses about the orbital axis. The action is mutual, however; the orbital circulation is also affected by the magnetic field due to the spin. The mutual interaction of the two magnetic moments can be described by saying that the axis of orbital motion and the axis of spin both precess around their resultant, the axis of total angular momentum. The electron thus has an orbital angular momentum characterized by the vector $\boldsymbol{l}$ and a spin angular momentum characterized by the vector $\boldsymbol{s}$, and both these vectors precess around their resultant $\boldsymbol{j}$.

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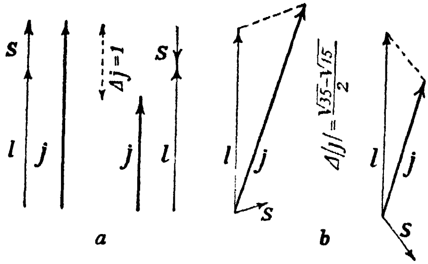
* Not to be confused with the symbol s used to denote energy levels with $l = 0$.

Alkali-like Atoms.—So far we have been considering an atom with a single electron. Our ideas can at once be extended to alkali-like atoms. Complete shells, such as are encountered in the inert gases, have no resultant angular momentum. Hence the total angular momentum of an alkali-like system is derived solely from the valency electron, and we can apply the above treatment directly. To each of the vectors $\boldsymbol{l}$, $\boldsymbol{s}$, and $\boldsymbol{j}$ we ascribe a quantum number (l, s, and j respectively) which can only change its value by integral amounts.



Figs. 17*a* and 17*b*.—Combination of the vectors $\boldsymbol{l}$ and $\boldsymbol{s}$ to give $\boldsymbol{j}$ for the case $l = 2$, $s = \frac{1}{2}$, $j = \frac{5}{2}, \frac{3}{2}$:

a, when $|\boldsymbol{v}| = v$;

b, when, as according to wave-mechanics, $|\boldsymbol{v}| = \sqrt{v(v+1)}$.

The effect of the spin of the electron is to modify the total angular momentum of the atom and hence also its energy. It will readily be appreciated that the energy may be either increased or diminished, according as the spin augments or opposes the remaining angular momentum of the atom. The complete calculation for a non-penetrating orbit gives the result that the change of energy W_s due to the electron spin is

$$W_s = \frac{Rhc\alpha^2 Z^4}{n^3 l(l+\frac{1}{2})(l+1)} ls \cos(\boldsymbol{l}, \boldsymbol{s}),$$

in which the constant α has the value $2\pi e^2/(hc)$. Thus it is necessary to know the value of $ls \cos(\boldsymbol{l}, \boldsymbol{s})$. Now the vector $\boldsymbol{j}$ is the vector sum of $\boldsymbol{l}$ and $\boldsymbol{s}$, i.e. $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$. From the geometry of the parallelogram of vectors we have

$$j^2 = l^2 + s^2 + 2ls \cos(\boldsymbol{l}, \boldsymbol{s})$$

or $$ls\cos(l, s) = \tfrac{1}{2}(j^2 - l^2 - s^2).$$

Note.—Bearing in mind the rule, justified by experimental observation, that the values of the quantum numbers can only change by integral amounts, we see at once that only the following combinations of the vectors are possible. The vector s must be either parallel or antiparallel to l, because $s = \frac{1}{2}$ and the difference between the two resulting quantum numbers, i.e. Δj in fig. 17*a*, must be integral. The two combinations give $j = l + s$ and $j = l - s$ respectively, i.e. $l + \frac{1}{2}$ and $l - \frac{1}{2}$, so that $\Delta j = 1$.

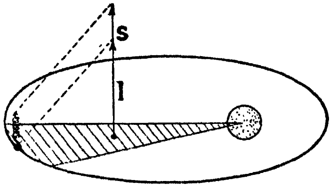


Fig. 18.—Addition of spin and orbital angular momentum to give the total angular momentum according to the Bohr model.

Vectors and Quantum Numbers.—In terms of the Bohr model the two possible orientations of the spin vector s (see note above) mean that the spin axis of the electron must be either parallel or antiparallel to the axis of orbital motion. The parallel case is illustrated diagrammatically in fig. 18.

In terms of the wave-mechanical model the meaning is rather different. Instead of the value $l\frac{h}{2\pi}$, the magnitude of the vector l is now $|l| = \sqrt{l(l+1)}\frac{h}{2\pi}$. Similarly we have in the wave-mechanical model $|s| = \sqrt{s(s+1)}\frac{h}{2\pi}$ and $|j| = \sqrt{j(j+1)}\frac{h}{2\pi}$.

The vector addition, which in the Bohr model has the form of fig. 17*a*, becomes modified in the wave-mechanical model to the form of fig. 17*b*. Here again $\Delta j = 1$ but

$$\Delta|j| = \left[\sqrt{\frac{5}{2}\cdot\frac{7}{2}} - \sqrt{\frac{3}{2}\cdot\frac{5}{2}}\right]\frac{h}{2\pi}.$$

In the wave-mechanical model the geometry of the vector parallelogram gives

$$\sqrt{l(l+1)}\sqrt{s(s+1)}\cos(l, s) = \tfrac{1}{2}[j(j+1) - l(l+1) - s(s+1)].$$

As in other cases, the wave-mechanical result is in complete agreement with experiment. Indeed, a corresponding modification of the older result had been introduced as a purely empirical correction before the wave-mechanical model had been discovered.

For the sake of simplicity of expression and diagrammatic representation, however, it is usual to adopt the form of vector addition shown in fig. 17*a*. This is used purely as a symbol, just as the chemist uses a hexagon as a symbol for benzene, it being borne in mind throughout that each of the vectors really has a magnitude of the wave-mechanical form $|\mathbf{v}| = \sqrt{v(v+1)}\,\frac{h}{2\pi}$ and that the quantity $ls\cos(\mathbf{l}, \mathbf{s})$ must really be replaced by the corresponding wave-mechanical quantity.

Splitting of the Energy Levels.—The change of energy W_s due to the spin of the electron has the value (see above)

$$W_s = \frac{Rhca^2Z^4}{n^3l(l+\frac{1}{2})(l+1)}\,\tfrac{1}{2}[j(j+1) - l(l+1) - s(s+1)].$$

In the case under consideration (only one electron) the only possible values of j are $l + \frac{1}{2}$ and $l - \frac{1}{2}$. Substituting these values and remembering that $s = \frac{1}{2}$, we obtain

$$W_s = \frac{Rhca^2Z^4}{n^3l(l+\frac{1}{2})(l+1)}\,\tfrac{1}{2}[\pm(l+\tfrac{1}{2}) - \tfrac{1}{2}].$$

We thus arrive at the quantitative result that each energy level associated with a particular value of l is split up into two levels. For one of these the electron spin augments the angular momentum of the atom; for the other it diminishes it. The energy in the former case is greater than in the latter, i.e. in the energy diagram the levels with higher j lie above those with lower j. (For exceptions see p. 333.) The case $l = 0$ is important. Here (as can be seen from the formula) there is only one value of W_s: energy levels for which $l = 0$ remain single.

This can also be deduced directly from the model. When the atom has no orbital angular momentum ($l = 0$), the vector $\mathbf{j}$ has the magnitude and direction of $\mathbf{s}$. There being no external field (an assumption that is made in all the above treatment), all directions in space are equivalent and there is no special direction for $\mathbf{j}$. The energy is thus independent of the direction of the spin vector $\mathbf{s}$, i.e. the energy level is single.

When $l \neq 0$, the difference between the two energy levels may be deduced at once from the formula given above. We obtain

$$\Delta W = h\Delta\nu = \frac{Rhca^2Z^4}{n^3l(l+1)}.$$

Here $\Delta\nu$ is the corresponding frequency difference. If we insert the numerical values of the constants, the corresponding wave-number difference (in cm.$^{-1}$) comes out to

$$\Delta\bar{\nu} = 5{\cdot}82\,\frac{Z^4}{n^3l(l+1)}.$$

An analogous result is obtained for penetrating orbits, due account being taken of the degree of screening at the different parts of the orbit.

Summing up, we may say that the theory that the observed splitting of the energy levels is due to electron spin gives a satisfactory explanation of the observed facts, in particular of the non-splitting of the S-terms for which $l = 0$. The calculated energy differences are in good agreement with the experimental values, both for the alkali energy levels with different l and n and also in a general way with the spark spectra of other systems with alkali-like electronic configurations.

For example, the splitting of the $3p$ energy level rises from 17·18 to 1889·5 cm.$^{-1}$ as we pass through the series Na, Mg^{+}, Al^{2+}, Si^{3+}, P^{4+}, S^{5+}, Cl^{6+}. This corresponds to effective nuclear charges which are in very good agreement with expectation.

The results obtained for H and He^{+} are also in accord with experiment. In this case it is found that the term-splitting effects, due on the one hand to the mass-variability of the electron and on the other hand to electron spin, lead to the coincidence of certain levels, e.g. the $2s$ state with $j = \frac{1}{2}$ and the $2p$ state with $j = \frac{1}{2}$.

The observed separations in the Balmer series are of the order of 0·3 cm.$^{-1}$, which is in agreement with the result of calculation, due account being taken of the fine structure (splitting) of the levels with $n = 3$, &c.

Behaviour in a Magnetic Field.—According to what has been said above, the atom may be regarded as a very complicated system of circulating electric charges, the different elements of which perform precessional motions around one another. It is clear that the behaviour of the whole system in an external magnetic field, where we shall have in addition precessional motions about the field direction, can hardly be treated in terms of the model, even though we adopt the simplified Bohr model. Fortunately it is found in most cases to be sufficient merely to know the quantum numbers mentioned above (p. 315) and to take account of the vectorial properties of the quantities with which they are associated.

The effect of an external magnetic field is determined principally by the field strength, as compared with the strength of the field produced in the interior of the atom by the motions of the constituent charges themselves. The precessional velocity is proportional to the field strength producing it. Consequently, if the external field strength is *small* in comparison with the internal, the precession of $\boldsymbol{l}$ and $\boldsymbol{s}$ around one another will be much faster than the precession around the direction of the external field. In this case there is still a physical significance in compounding $\boldsymbol{l}$ and $\boldsymbol{s}$ to give the resultant angular momentum vector $\boldsymbol{j}$, and then considering the precession of $\boldsymbol{j}$ around the field direction.

If, on the other hand, the external field strength is *large* in comparison with the internal, then both $\boldsymbol{l}$ and $\boldsymbol{s}$ precess very rapidly around the field direction and have to be considered independently. It is possible to decide in the following way which of these two states of affairs is realized in a given case. The frequency of precession is given directly by the frequency difference between the energy levels with and without the field. The doublet separation gives directly the frequency of precession of $\boldsymbol{l}$ and $\boldsymbol{s}$ around $\boldsymbol{j}$. If the application of the external field causes a splitting of the energy levels (p. 203) which is small compared with the doublet separation in the absence of the field, then we have the first state of affairs referred to above: the behaviour in presence of the field can be interpreted as due to the precession of $\boldsymbol{j}$ around the field direction. This is the so-called (anomalous) ZEEMAN effect. If, on the other hand, the applied field is so strong that the splitting it causes is large compared with the field-free doublet separation, then the vector $\boldsymbol{j}$ loses its physical significance and it is necessary to consider the behaviour of $\boldsymbol{l}$ and $\boldsymbol{s}$ separately. This is the PASCHEN-BACK effect. These two states of affairs are, of course, limiting cases. In between them lie intermediate sets of conditions which participate to some extent in the characteristics of both extremes.

We shall first consider the case of weak external magnetic fields (ZEEMAN effect). The magnetic behaviour of the atom is determined by its magnetic moment. According to p. 208, the magnetic moment associated with the orbital motion is $l\mu_0$, where μ_0 stands for the magneton $eh/(4\pi mc)$. The magnetic moment μ_e possessed by the electron on account of its spin is one magneton. Since $s = \frac{1}{2}$, we may write $\mu_e = 2s\mu_0$. Thus the ratio of magnetic moment to angular momentum is twice as great for the spin of the electron as for its orbital motion (see p. 209). (For reference to this in connexion with the experiments of BARNETT and EINSTEIN and DE HAAS, see Vol. III, p. 446.) The total magnetic moment of the atom (assumed to be a one-electron or alkali-like system) is obtained by combination of the orbital moment and the spin moment. Both of these, however, precess around $\boldsymbol{j}$. We may resolve the individual moments into components in the direction of $\boldsymbol{j}$ and at right angles to this direction. Because of the precession of $\boldsymbol{l}$ or $\boldsymbol{s}$ around $\boldsymbol{j}$, the components at right angles to $\boldsymbol{j}$ rotate around $\boldsymbol{j}$ and continually alter their directions. Hence their time average is zero (provided there is no external field or only a weak external field). If $\boldsymbol{j}$ were produced simply by a circulatory current, the total magnetic moment would be $j\mu_0$. Owing to the contribution of the spin and the consequent precessional motions, however, the total magnetic moment is $jg\mu_0$.* This is equal to the sum of the resolved parts of the component moments in the direction of $\boldsymbol{j}$, i.e. we have

$$jg\mu_0 = [l\cos(\boldsymbol{l},\boldsymbol{j}) + 2\cos(\boldsymbol{s},\boldsymbol{j})]\,\mu_0.$$

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* The factor g is often referred to as LANDÉ's splitting factor, from LANDÉ, who discovered the correct formula for g empirically and gave a classical calculation leading to a similar result.

Inserting the values for the cosine terms (see p. 314), we obtain for g the value

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$

Thus the atom may be regarded as a magnetic spinning top with the magnetic moment $jg\mu_0$ and the mechanical angular momentum $j\frac{h}{2\pi}$. The factor g may be greater than unity, since the magnetic moment of the spinning electron is twice as great as that for a circulatory current of the same mechanical angular momentum.

We can now at once understand the behaviour of the silver atoms in the Stern-Gerlach experiment (p. 207). The silver atom has an alkali-like structure (pp. 4 and 342). As for all alkali-like atoms, the ground state has $l = 0$ (i.e. the lowest term is an S-term), and therefore j has the value $\frac{1}{2}$. Consequently we must expect the orientations in the magnetic field to be as shown in fig. 63, p. 205, for half-integral j-values. The experimentally-observed splitting into two in the magnetic field (see figs. 65 and 66, p. 207) and the complete *absence* of a trace corresponding to undeflected atoms are well explained by the above argument. The measured value of the magnetic moment (one magneton) indicates that we must indeed ascribe this value to the electron spin.

As explained on p. 203, the number of possible orientations of the vector j in the magnetic field is finite and equal to $(2j + 1)$. We will characterize by the so-called magnetic quantum number m the projection of the vector j on the direction of the applied field. The precessional energy (calculated in the way described on p. 204) is then

$$W_m = mg\mu_0 H = mgL.$$

Here $L = \mu_0 H$ is called the Lorentz unit. This theory is successful in accounting very exactly for the observed Zeeman effects of the alkalis. It makes it clear why the so-called normal triplet splitting is not found with these atoms (see fig. 20, p. 319).

The Paschen-Back Effect.—When the external magnetic field is made very strong, each of the vectors l and s separately takes up certain possible orientations relative to the field direction. In the case of s there are two possible orientations, characterized by the quantum numbers $m_s = \pm\frac{1}{2}$. In the case of l there are $(2l + 1)$ possible orientations, characterized by the quantum number m_l, which may have any integral value from $-l$ to $+l$. Since the ratio of magnetic moment to angular momentum is twice as great for s as for l, the precessional velocity of s is twice as great as that of l.

The different energy states of the atom are here given by the sums of the magnetic energies and the energy of interaction of s and l. The former are $W_m{}^s = 2m_s\mu_0 H$ and $W_m{}^l = m_l\mu_0 H$. The latter is of the form given on p. 313, but in consequence of the separate precessions of $\boldsymbol{l}$ and $\boldsymbol{s}$ around the field direction the average value of $\cos(\boldsymbol{l}, \boldsymbol{s})$ is equal to $\cos(\boldsymbol{l}, \mathbf{H}) \cos(\boldsymbol{s}, \mathbf{H})$, so that $ls \cos(\boldsymbol{l}, \boldsymbol{s}) = m_l m_s$. The total

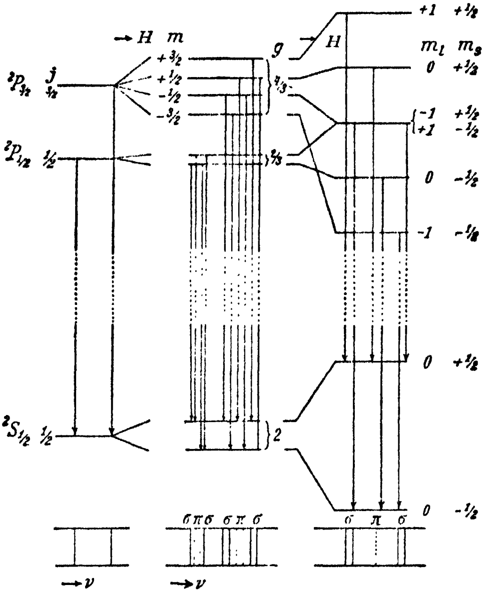

Fig. 19.—Splitting of the D lines of sodium by an applied magnetic field
On the left, no field; centre, weak field. On the right, strong field.

energy of the atom (relative to the energy in the absence of an applied field) may therefore be written $W_{PB} = (m_l + 2m_s + a m_l m_s)\mu_0 H$. The subscript PB stands for Paschen-Back. Thus in strong fields the energy levels are quite different from those in weak fields. Hence the splitting patterns of the spectral lines are different in the two cases; for the lines are due to transitions between the energy levels (see figs. 19 and 20). As indicated in fig. 19, a gradual change-over from the one type of pattern to the other can be achieved by gradually increasing the strength of the applied field.

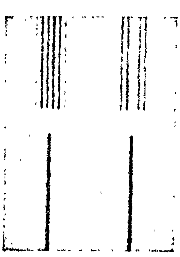

Fig. 20.—Splitting of the D lines of sodium in a weak magnetic field.

[From Back-Landé, *Zeeman-Effekt* (Springer, Berlin).]

An important point is that the principal quantum number n, being a scalar, does *not* occur in the formulæ for the influence of the field. Hence it follows that the type of Zeeman effect must be the same for all the lines of a series. This furnishes very valuable assistance in the search for series relationships. It is also important that the *number* of energy levels is the same (namely $4l + 2$) for weak and strong fields. This can easily be seen by working out the possibilities.

7. Possible Atomic States. Selection Rules

Designation of Atomic States.—The quantum numbers n, l, j and m hitherto used refer to the states of a single electron. In designating the state of the electron it is customary to use, instead of the number l, the corresponding letter s, p, d, &c., ascribed to the l-value in accordance with the scheme given on p. 311. Thus, for example, $4d$ denotes an electron state in which the electron moves in an orbit with principal quantum number $n = 4$ and with an orbital angular momentum corresponding to $l = 2$, i.e. $|l| = \sqrt{2(2+1)}\frac{h}{2\pi}$. In the case of atoms with only one electron, the state of the whole atom is thereby defined; if the one electron has the quantum numbers j and l, the total and orbital angular momenta of the whole atom have values corresponding to these numbers respectively.

In the case of atoms with more than one electron the total and orbital angular momenta of the whole atom are quite different from those of the individual electrons, for the contributions of these electrons may combine together in quite different ways according to the particular electronic configuration. It therefore becomes necessary to distinguish between those quantities which apply to the whole atom and those which apply to the individual electrons. **It is customary to use capital letters to denote the quantities describing the atom as a whole.*** Thus the term symbol F denotes an atomic state in which the vector sum of all the orbital angular momenta of the individual electrons is given by $|\mathbf{L}| = \sqrt{3(3+1)}\frac{h}{2\pi}$, i.e. in which the total orbital quantum number is $L = 3$.

All that we have to do, therefore, is to replace the small letters used for atoms with one electron by capital letters. It is further customary to denote the multiplicity of a state by the appropriate number written as a superscript in front of the letter indicating the value of L. This is done even for S-states (which according to p. 312 are all single), in order to make their membership of a certain multiplet system of terms clear. For with atoms having more than one electron there are several systems with different term multiplicities; for example, the alkaline earths (fig. 4, p. 283) have a singlet system and a triplet system. Then the total angular momentum quantum number is written as a subscript after the main term symbol. For instance, $^2P_{\frac{3}{2}}$ (which is read: doublet P three-halves) denotes an atomic state belonging to a doublet system (this is connected with the orientation of the spin vectors (p. 312)), the vector sum of the individual orbital angular momenta having the quantum number $L = 1$ (since the state is a P-state), and the total angular momentum having the quantum number $\frac{3}{2}$.

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* According to this convention, the vector sum of the spin angular momentum vectors of the individual vectors would be described by a quantum number S. In order to prevent confusion with the term symbol S (denoting a term with total orbital angular momentum number $L = 0$), the total spin number is denoted in this book by the symbol Σ.

In the alkali metal atoms (and in alkali-like atoms) the state of the atom as a whole is determined by the state of the single valency electron only.

The total orbital angular momentum of a complete shell, such as is found in the inert gases, is in the ground state given by $L = 0$. As will be shown later (p. 333), the spin vectors of the individual electrons orient themselves in such a way that the total angular momentum is also given by $J = 0$. Hence the ground state of the Na atom must be a $4^2S_{\frac{1}{2}}$ state; for the term diagram shows that the lowest level of the valency electron is $4s$. The orbital angular momentum is zero, because that of the atomic core is zero and that of the valency electron in its s-state ($l = 0$) is also zero (p. 311). The total angular momentum quantum number, which here is due only to the spin of the valency electron, is $J = \frac{1}{2}$. The term belongs to a doublet system.

Table XXIV gives the possible excited states which can be assumed by an atom with one electron (or by an alkali-like atom), inclusive of the various possible spatial orientations relative to an applied magnetic field of not too great strength.

Selection Rules.—On several previous occasions (e.g. pp. 196 and 285) it has been remarked that under ordinary conditions of excitation *all* the conceivable combinations of energy levels do *not* appear as spectral lines, i.e. that transitions from one energy level to *every* other energy level by absorption or emission of radiation are not possible. It is found that the transitions which are possible are determined by quite simple selection rules involving the quantum numbers which characterize the states in question. The following rules for one-electron or alkali-like systems may be derived from the experimental data:

1. The change of the principal quantum number n is not subject to any restriction, but the probability of a transition from the state n_2 to the state n_1 becomes smaller with increase of $\Delta n = n_2 - n_1$. This is an expression of the fact that the intensity of the lines of a series falls off progressively as we pass towards higher members of the series.

2. As regards the change of the orbital angular momentum quantum number l, only those lines are observed for which l changes by $+1$ or -1, i.e. $\Delta l = \pm 1$. Thus under normal conditions (absence of strong external fields) an atomic state characterized in the wave-mechanical model by a certain wave function can only pass over into a state characterized by a wave function with the next proper value.

3. Only those lines are observed for which the total angular momentum quantum number j either does not change or changes by $+1$ or -1. If the initial state has $j = 0$, then the transition to a final

TABLE XXIV.—POSSIBLE STATES OF A ONE-ELECTRON SYSTEM

Principal quantum number	n	1	2			3					4						
Orbital angular momentum	l	0	0	1		0	1		2		0	1		2		3	
Total angular momentum	j	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
Magnetic quantum number	m	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{3}{2}$ to $-\frac{3}{2}$	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{3}{2}$ to $-\frac{3}{2}$	$+\frac{3}{2}$ to $-\frac{3}{2}$	$+\frac{5}{2}$ to $-\frac{5}{2}$	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{1}{2}$ $-\frac{1}{2}$	$+\frac{3}{2}$ to $-\frac{3}{2}$	$+\frac{3}{2}$ to $-\frac{3}{2}$	$+\frac{5}{2}$ to $-\frac{5}{2}$	$+\frac{5}{2}$ to $-\frac{5}{2}$	$+\frac{7}{2}$ to $-\frac{7}{2}$
Term symbol		$1^2S_{\frac{1}{2}}$	$2^2S_{\frac{1}{2}}$	$2^2P_{\frac{1}{2}}$	$2^2P_{\frac{3}{2}}$	$3^2S_{\frac{1}{2}}$	$3^2P_{\frac{1}{2}}$	$3^2P_{\frac{3}{2}}$	$3^2D_{\frac{3}{2}}$	$3^2D_{\frac{5}{2}}$	$4^2S_{\frac{1}{2}}$	$4^2P_{\frac{1}{2}}$	$4^2P_{\frac{3}{2}}$	$4^2D_{\frac{3}{2}}$	$4^2D_{\frac{5}{2}}$	$4^2F_{\frac{5}{2}}$	$4^2F_{\frac{7}{2}}$
Number of states		2	2	2	4	2	2	4	4	6	2	2	4	4	6	6	8
Total number of states ..		2	8			18					32						
Shell		K	L			M					N						
Sub-groups			L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}

state having $j = 0$ is forbidden. The selection rules may here be written $\Delta j = 0$ or ± 1; $0 \rightarrow 0$ forbidden.

4. Only those lines are observed for which the magnetic quantum number m either does not change or changes by $+1$ or -1, i.e. $\Delta m = 0$ or ± 1.

5. In the presence of very strong magnetic fields, the magnetic quantum number of the orbital angular momentum either does not change or changes by $+1$ or -1, i.e. $\Delta m_l = 0$ or ± 1. The magnetic quantum number of the spin in general remains unchanged, i.e. $\Delta m_s = 0$.

These selection rules furnish extremely important assistance in the allocation of observed spectral series to the proper quantum numbers; for in complicated spectra it is a difficult matter to determine relationships between frequencies of series limits, &c., such as hold for the alkali spectra. For the extension of the rules to atoms with more than one electron, see p. 330. It is important to note that transitions which contravene the rules are sometimes observed; but the intensities of such lines are usually very small in comparison with the normal lines.

Feeble lines of this kind, which contravene the selection rules, are found particularly in absorption spectra under favourable conditions of observation. Further, the above selection rules also lose their strict validity in the presence of strong applied fields. Thus in intense *electric* fields lines can be observed for which $\Delta l = 2$. As an example we may mention the series $2^1S - m^1D$ and $2^3S - m^3D$ observed by STARK under the influence of a strong electric field. On the other hand, the selection rule for j is not affected by strong electric fields, though in strong *magnetic* fields deviations are observable.

Considerations of the kind put forward on p. 196 make it possible to understand in terms of BOHR's correspondence principle why Δl is normally not greater than 1; for the harmonics do not occur in the Fourier analysis of the orbital motion. The presence of external fields causes a non-uniform precession of the orbit, so that harmonics occur in the Fourier analysis and the observed transitions with $\Delta l > 1$ under these circumstances become intelligible. The vector j has the property of being the axis around which the vector l (i.e. the axis of the orbital motion in the BOHR model) precesses. Since the precession of l around j is uniform, only the coefficients $+1$ and -1 occur in the Fourier analysis for the projection as seen in the direction of j. In the projection on the direction of j there is no periodic motion at all: the coefficients are zero. The three corresponding transitions are therefore $\Delta j = 0, \pm 1$. Since the precession is disturbed by strong magnetic fields, values of Δj corresponding to harmonics are in these circumstances possible.

Analogous considerations also hold (see p. 205) for the magnetic quantum numbers.

The selection rule for the total angular momentum can also be derived from consideration of the interaction between the radiation and the atom, if we make use of the fact that the angular momentum must be conserved for the whole system, atom + radiation field. Examples of the fulfilment of the selection rules may be sought in the term diagrams, e.g in figs. 3–7 (pp. 281 to 288).

8. Atoms with More than One Electron

The purpose of a model of an atom with more than one electron is clearly to account for the behaviour of the whole atom in terms of the individual electrons—the arrangement of their orbits or their charge distribution, their number, the directions of their spins and the interactions of the various quantities associated with them. Since even for one electron the various precessional motions make the conditions very complicated, a direct representation of the motions in atoms of complex structure is impracticable, even though the simplified Bohr model is adopted. However, the vector model still allows of deductions (at least so far as the multiplicities of the atomic states are concerned) which lead to a consistent explanation of the observed properties (spectral lines, spectral behaviour in a magnetic field, magnetic properties, chemical properties, &c.).

Systems with Two Electrons.—First of all we shall consider a system with two valency electrons, e.g. the helium atom or (as we explained above) an alkaline earth atom such as calcium. What multiplicities of the electronic configuration are possible? Take first the mean distance from the nucleus, i.e. the principal quantum number. In the ground state the electrons occupy orbits with the smallest possible quantum number n. In each of the two cases quoted as examples above the chemical properties and position in the periodic table indicate that the two electrons are practically equivalent, so that in He both have $n = 1$ and in Ca both have $n = 3$. What happens when the atom is excited? Do both the electrons take up energy and move in orbits of higher n, or is the excitation energy always concentrated on one electron? As will be appreciated from the subsequent discussion, consideration of the spectra shows that in general (even in still more complicated atoms) the energy given out or taken in in a transition is emitted or absorbed by one electron only, i.e. only one electron changes its state in the process giving rise to a spectral line. Cases do, however, occur (actually observed for the alkaline earths) in which both electrons change their states simultaneously, so that the $h\nu$ value of the emitted line is the sum of the energy changes of the two electrons, i.e. the energy change of the whole atom. Excitation of the atom *by stages* gives every possible state of simultaneous excitation of both electrons, except for one special restriction which will be discussed on p. 333.

Bearing this restriction in mind, we consider two electrons occupying orbits with *different* principal quantum numbers n. Suppose that both the orbits have $l = 0$: or in other words (introducing the nomenclature used for the alkali spectra), suppose that both electrons are in s-states (so-called s-electrons). What are the possible arrangements? Since both orbits are without angular momentum, all mutual orientations of the orbits are equivalent. We are left with the possibilities of orientation of the spin vectors. In the case under consideration the total angular momentum is due entirely to the spins: we have $s_1 = s_2 = \frac{1}{2}$, and j must be either 1 or 0. In the simple vector model the value $j = 1$ corresponds to similarly directed spins, the value $j = 0$ to oppositely directed spins (see fig. 21*a*). Thus only two atomic states are to be expected.

Note.—The wave-mechanical value of the magnitude of the spin vector is $|\mathbf{s}| = \sqrt{s(s+1)}\,\frac{h}{2\pi}$ instead of $s\frac{h}{2\pi}$ (compare p. 314). Hence the composition of similarly directed or "parallel" spins is in reality as shown in fig. 21*b* instead of as shown in fig. 21*a*. However, we adopt the convention of symbols explained on p. 314 and for simplicity describe the system in terms of fig. 21*a*, using $|s| = s\frac{h}{2\pi}$. This symbolic representation may be interpreted at any stage by inserting the wave-mechanical values.

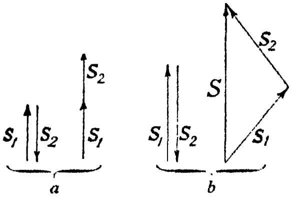


Fig. 21.—Combination of the spins of two electrons:
a, when $|v| = v$;
b, when, as according to wave-mechanics, $|v| = \sqrt{v(v+1)}$.

We now consider a system in which only one electron is in an *s*-state (i.e. $l_1 = 0$), the other being in a state with some other *l*-value. The atomic state is thus characterized by s_1, $l_1 = 0$, s_2, and l_2. Before we can decide about the possibilities we must inquire into the nature of the interactions between the different vectors. Must we take account (as in the one-electron system) of the coupling between the orbital and spin angular momenta of the second electron, neglecting the effect of the first electron? Or is the coupling between the two spins the predominant factor? A decision between these alternatives can be obtained from the spectra of atoms with two valency electrons. For this purpose we consider the difference in energy between corresponding states with different term multiplicities. If this difference is smaller than (or at most of the same order as) the difference due to reversal of spin relative to orbital angular momentum (e.g. the difference between the sodium D lines), then the first alternative is realized. If, on the other hand, the difference is larger than that due to reversal of spin relative to orbital angular momentum (see the formula, p. 315), then the second alternative is realized, i.e. the coupling between the spins of the two electrons is stronger than the coupling between the spin and the orbital motion of the second electron. Actually the positions of the terms of helium (fig. 6, p. 286) show that this latter state of affairs is the true one (see below). Thus the spin of the first electron has an effect upon the second like the Paschen-Back effect observed in a very strong magnetic field: the spin vector $\mathbf{s}_2$ behaves as if $\mathbf{l}_2$ did not exist. The spin vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ both precess around the direction of their resultant, which we will denote by **S** and call the **resultant spin vector** of the atom. The corresponding quantum number will be written Σ (see footnote to p. 320).

Adopting the notation referred to on p. 320, we denote by capital letters all the quantities which refer to the atom as a whole. Thus the total angular momentum **J** of the atom is the resultant of the vectors **L** and **S**, which are themselves the resultant orbital and spin angular momenta respectively of the whole atom. In the particular case at present under discussion $L = l_2$.

In a two-electron system Σ may have either of the values 0 or 1 (antiparallel or parallel spins). When the spins are antiparallel, there is in our case only one value of J, namely l_2. When the spins are parallel, J may have the values $l_2 + 1$, l_2, and $l_2 - 1$. Hence we may expect a singlet and a triplet system. In helium the electronic configuration under discussion (i.e. $l_1 = 0$) is actually realized (for the proof of this —from the term relationships—see below), and a singlet and a triplet system are in fact observed (fig. 6, p. 286). The energy differences between corresponding levels (equal principal quantum number and equal orbital angular momenta) are, as may be seen from fig. 6, p. 286, much greater than the differences between the three components of a triplet term. This constitutes the experimental justification for the above assumption of a very strong coupling of the two spins.

This strong coupling cannot be explained by classical considerations; at most an effect of the same order as the coupling of spin and orbital angular momentum would be expected. The real reason lies in the wave-mechanical resonance mentioned on p. 274. The conditions outlined above for helium formed the experimental clue by which HEISENBERG was led to the discovery of the phenomenon of wave-mechanical resonance.

When the two electrons have the l values l_1 and l_2, these combine to give a resultant L whose value may range from $| l_1 - l_2 |$ to $l_1 + l_2$. The resultant spin number Σ may again be either 0 or 1. For $\Sigma = 0$ we have $J = L$, i.e. all the L-states are single. For $\Sigma = 1$ we have $J = L + 1$, L or $L - 1$, i.e. the L-states are triple, except when $L = 0$ (S-state); for if $L = 0$ the spin Σ can have no special orientation and $J = \Sigma$. Of course since **J** is the total angular momentum of the atom, its value must be either positive or zero.

We may now briefly consider the possible states which may arise when two electrons are present. Take, for example, the case where one electron is a p-electron ($l_1 = 1$) and the other is a d-electron ($l_2 = 2$). In the first place we have to distinguish between two sorts of states, singlet and triplet. These correspond respectively to antiparallel and parallel electron spins. Consider first the singlet states, for which $\Sigma = 0$. If the orbital circulation of the p-electron is exactly opposed to that of the d-electron, we have $L = 3 - 2 = 1$. Since $\Sigma = 0$,

$J = 1$. The atom is in a $^1P_1$ (singlet-P-one) state. If the two orbital angular momentum vectors are so inclined to one another that $L = 2$, we have $J = 2$, and the state is $^1D_2$. If the two orbital angular momentum vectors are parallel (for the wave-mechanical meaning of " parallel " see fig. 21*b*, p. 325), we have $L = 2 + 1 = 3$, $J = 3$, and the state is $^1F_3$.

Now consider the states with parallel spins, for which $\Sigma = 1$. Take the case where the orbital angular momenta are antiparallel, i.e. $L = 3 - 2 = 1$. There are now three possibilities: the resultant spin vector may combine with $\mathbf{L}$ to give $J = 0$, 1, or 2. The first of these possibilities is realized when the resultant spin vector is antiparallel to $\mathbf{L}$, i.e. in the Bohr model when the spins of both electrons are antiparallel to the orbital angular momentum of the *d*-electron. This gives one of the three components of a triplet state, namely $^3P_0$. The second component ($J = 1$) is denoted by $^3P_1$. The third component ($J = 2$) is realized when the resultant spin vector is parallel to $\mathbf{L}$, i.e. in the Bohr model when the spins of both electrons are parallel to the orbital angular momentum of the *d*-electron. This component is $^3P_2$. Similar considerations hold for other values of L. If the two orbital angular momenta are so inclined as to give $L = 2$, we get three D-states, viz. $^3D_1$, $^3D_2$, and $^3D_3$. Finally, if the two orbital angular momenta are parallel ($L = 3$), we get three F-states, namely, $^3F_2$, $^3F_3$, and $^3F_4$. In the state $^3F_4$ the two spins and the two orbital angular momenta are all parallel. For the energies of the different states see p. 330.

The above symbols are not sufficient to determine the states of the atom completely, for they tell us nothing about the principal quantum numbers n of the electrons. These are quite unrestricted. Hence in order to describe a given excited state completely it is necessary to state the principal quantum number of each electron. This is done by writing the states of the individual electrons before the main symbol. Suppose that in the above example the *p*-electron of the excited helium atom occupies an orbit with $n = 2$ and the *d*-electron an orbit with $n = 3$. The $^3F_4$ state is then written $2p \,.\, 3d \,.\, {}^3F_4$. If two electrons have the same n, a superscript 2 is written after the letter denoting the l-value. For example, two electrons with $n = 1$ and $l = 0$ would be written $1s^2$.

Using the symbol (A) to denote the 18 electrons forming the completed shells of argon, the symbol for the ground state of Ca (20 electrons) may be written $(A) \,.\, 4s^2 \,.\, {}^1S_0$.

Atoms with More than Two Valency Electrons.—We simply have to extend the scheme given above for two electrons. Here again the most important question is that of the interaction or coupling between the spins and orbital angular momenta of the different electrons. The majority of spectra hitherto investigated indicate, as in the two-electron case, a strong coupling between the individual spin vectors on the one hand and between the individual orbital angular momentum vectors on the other hand. Hence the state of the atom may be characterized by a resultant spin vector **S** (corresponding quantum number Σ) and a resultant orbital angular momentum vector **L** (corresponding quantum number L) which combine to give a total angular momentum **J** (corresponding quantum number J). This type of interaction, called **Russell-Saunders coupling,** may be symbolized thus: $\{(s_1, s_2, s_3 \ldots), (l_1, l_2, l_3 \ldots)\} = (\mathbf{S}, \mathbf{L}) = \mathbf{J}$.

Under certain circumstances, however, the coupling between the spins of the electrons and their orbital angular momenta may even be stronger than that between the spins themselves. In the extreme case the individual electrons behave as if there were no mutual interaction between them. If this is so, each electron may be considered separately (as on p. 312 for a single electron), and its contribution j_i to the total angular momentum may be obtained by combination of its individual s_i and l_i. The vector sum of all these individual contributions j_i then gives the total angular momentum **J**. This may be symbolized thus: $\{(s_1, l_1), (s_2, l_2), (s_3, l_3) \ldots\} = (j_1, j_2\ j_3, \ldots) = \mathbf{J}$, and the phenomenon is called **jj-coupling**. It occurs, for example, in connexion with X-ray spectra and the spectra of the heavier atoms. The two types of coupling mentioned above are limiting types, between which the whole range of intermediate types may occur. Except in the extreme cases, however, the treatment of the problem is very difficult.

9. Term Multiplicities

The empirical facts of the doublet nature of all the terms (except the S-terms) of alkali-like systems and of the singlet and triplet nature of all the terms (in the latter case, with the exception of the S-terms) of the alkaline earth atoms are explained as due to the different possible orientations of electron spin, either relative to orbital angular momentum or to another electron spin. According to this explanation, each energy level of given orbital angular momentum is split up into a number of multiplet components equal to the number of possible orientations. This number is referred to as the *multiplicity of the term.* In general the resultant spin quantum number Σ can have the values $\sum_i(\pm s_i)$. For three electrons, for example, we have $\Sigma = \frac{1}{2}$ or $\frac{3}{2}$; for four electrons, $\Sigma = 0$, 1, or 2. If $\Sigma = 2$, there are five possible orientations giving integral values of J for each value of L > 2. Hence each of the terms with L > 2 is split up into five components of slightly differing energies: we have a so-called quintet term. Even for complicated atoms the S-states must always be single; for here L $= 0$ and the total angular momentum of the atom is due entirely to the resultant of the spins, for which all orientations are equivalent. By investigating a few examples it is easily seen that in general J can have all values from $| L - \Sigma |$ up to $| L + \Sigma |$, successive J-values differing of course by unity. It is also easily seen that *the maximum multiplicity* r *for a given value of* Σ *is* $r = 2\Sigma + 1$. This maximum multiplicity is included in the term symbol even for those terms whose L-values do not permit of the attainment of the maximum (see the remark on the S-terms, p. 320). For example, in a quintet system ($\Sigma = 2$) the $^5S_2$ term is single and the ^5P term only triple ($^5P_1$, $^5P_2$, $^5P_3$). Not until ^5D do the terms actually become quintets. The reader is recommended to practice applying these ideas by working out examples in detail, drawing the vectors if necessary. From the multiplicity r which is always given in the symbol of a term it is always possible to deduce the resultant spin quantum number Σ from the relation $\Sigma = \frac{1}{2}(r - 1)$.

We see, therefore, that the occurrence of the doublet and quartet systems in the third group of the periodic table (compare Table XXI, p. 299) is due to the presence of the *three* valency electrons. For here the values of Σ are $\frac{1}{2}$ or $\frac{3}{2}$, whence $r = 2\Sigma + 1 = 2$ or 4. In general the above relationships show that an even number of valency electrons corresponds to an odd term multiplicity and an odd number of valency electrons corresponds to an even term multiplicity. Moreover, it follows that the term multiplicities of the successive spark spectra of a given element must show an alternation between odd and even, because one valency electron is lost on passing from each stage of ionization to the next. Table XXV gives the multiplicities actually observed in the successive stages of ionization of chlorine.

TABLE XXV.—TERM MULTIPLICITIES IN THE SUCCESSIVE SPARK SPECTRA OF CHLORINE

Ion Number of Electrons	Cl^{6+} $11 = 2 + 8 + 1$	Cl^{5+} 12	Cl^{4+} 13	Cl^{+++} 14	Cl^{++} 15	Cl^{+} 16
Multiplicity	doublet	singlet triplet	doublet quartet	singlet triplet	doublet quartet	singlet triplet

Here we cannot discuss in full how the theory accounts for even the finest details of the splitting of lines in magnetic fields and of the multiplet structure of lines. This will become evident from the examples which will be encountered from time to time. It may be remarked here that, though the energy state of an atom is uniquely determined by the arrangement of the spins and orbital motions of all its electrons, yet in complicated cases it is not possible to deduce this arrangement uniquely from the knowledge of the energy state. Thus, for example, for Gd^{+++} there are ten possible arrangements of the vectors which may give a ^2F term.

Selection Rules.—The rules given on p. 321 for one electron still hold good for the corresponding quantum numbers L, Σ, and J of a system with more than one electron. Since, however, two electrons may take part simultaneously in a process which gives rise to a spectrum line, the case $\Delta L = 0$ is possible in addition to $\Delta L = \pm 1$. When two electrons are involved in this way, $\Delta l_1 = \pm 1$ for the first and (as was shown by HEISENBERG) $\Delta l_2 = 0$ or ± 2 for the second. Usually Σ does not change in a spontaneous transition. This corresponds to the fact, already mentioned on p. 285, that transitions between singlet and triplet systems (and the like) occur very seldom. If, however, the interaction between **S** and **L** is large (as is the case, for example, in the more complicated atoms), then changes of Σ may occur. Thus in the case of Hg (see the term diagram on p. 284) these transitions between terms belonging to systems of different multiplicities are very frequent and the corresponding spectrum lines are fairly intense.

Relative Positions of the Terms.—As regards the relative positions of the terms *for a given set of values of n and l*, a good general idea can be obtained in many cases with the help of the following rules, which were discovered by SLATER and HUND:

1. The more nearly similar the spin directions, the lower is the term (i.e. the energy) of the atom. Thus the terms of higher multiplicity lie lower than the corresponding terms of lower multiplicity. (See, for example, figs. 4 and 5, pp. 283 and 284.)

2. The more nearly similar the directions of the orbital angular momentum vectors, the lower is the term of the atom. Thus amongst the terms of a given multiplicity, those with larger L usually lie lower than those with smaller L (see fig. 3, p. 281, and fig. 7, p. 288). In this connexion it must be remembered that the rule only applies to terms with the same electronic configuration as regards *n* and *l*. The rule does not hold for helium, as is seen from fig. 6, p. 286.

3. The more nearly similar the directions of the spin and orbital angular momentum vectors, the higher is the term of the atom. Thus terms with smaller J lie lower than those with larger J. This rule does not hold, however, unless the outermost electron group is less than half completed (see p. 333). Otherwise the rule is reversed and the term positions are said to be *inverted*. Inversion is met with in X-ray spectra.

10. The Pauli Exclusion Principle

The properties of helium show that both its electrons are in the 1*s* state, so that the formula (ground state) is $1s^2 . S$. The S-term would be expected to have two values, according as the spins of the two electrons are parallel or antiparallel; and the two values should not lie very far apart. Inspection of the term diagram shows, however, that there is only *one* S-term in the neighbourhood of the ground state. This is the $^1S_0$ term, corresponding to the electronic configuration in which the two spins are antiparallel. The configuration in which the spins are parallel *does not exist.* A similar state of affairs is found in other cases. Considerations of this kind led to the formulation of an empirical rule—the so-called **exclusion principle** (Pauli, 1925) —which has proved extremely fruitful. The exclusion principle (also called the Pauli principle) may be expressed as follows:

It is impossible for two electrons in an atom to be identical as regards all their quantum numbers.

The application of this principle requires a certain amount of consideration. In most cases the coupling between the electrons is so strong that only the quantum numbers n and l can be ascribed to the individual electrons, the state of the atom as a whole being characterized by L and J. In order to bring out the individuality of the electrons, it is necessary to imagine such a strong magnetic field applied to the system that (in accordance with p. 318) the coupling between the electrons is overcome. The state of any particular electron can then be described by the quantum numbers n, l, m_l, and m_s. If the coupling between spin and orbital angular momentum is not overcome, the numbers n, l, j, and m must be used.

The non-existence of the 1^3S state of orthohelium can accordingly be explained as follows. If $n = 1$ and $l = 0$, then in a strong field the only possible value of m_l is zero; but m_s can have the values $\pm\frac{1}{2}$. Thus there are only two possible sets of the four quantum numbers when $n = 1$ and $l = 0$. Hence with two electrons there can only be *one* possible atomic state, namely, that in which one electron has one of the sets of numbers and the other has the other set. The two electrons are then respectively characterized as follows: (1) $n = 1$, $l = 0$, $m_l = 0$, $m_s = +\frac{1}{2}$, and (2) $n = 1$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$. The two spins are antiparallel. No other state of the atom is possible for $n = 1$ and $l = 0$; for parallel spins are excluded by the Pauli principle.

Further, it is clear that two is the maximum number of electrons with $n = 1$, $l = 0$ which the atom can have; for a greater number would mean that two (or more) would necessarily be identical as regards all their quantum numbers, which would violate the Pauli principle. The whole periodic table and with it the whole of the chemical relationships of the elements follow from considerations of this kind (see p. 334 *et seq.*). Table XXVI gives the possible states for different values of n and l up to $n = 4$. This table gives the same number of possible states as Table XXIV (p. 322), in accordance with the fact (p. 319) that the number of energy levels is the same in a weak magnetic field as in a strong magnetic field and therefore does not depend upon the nature of the coupling.

TABLE XXVI.—POSSIBLE ELECTRONIC STATES FOR $n = 1$ TO $n = 4$

n	1	2				3									4															
l	0	0	1			0	1			2					0	1			2					3						
m_l	0	0	+1	0	−1	0	+1	0	−1	+2	+1	0	−1	−2	0	+1	0	−1	+2	+1	0	−1	−2	+3	+2	+1	0	−1	−2	−3
m_s	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$
	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
Number of states	2	2	6			2	6			10					2	6			10					14						
Total number	2	8				18									32															
Shell	K	L				M									N															

Limitation of Term Multiplicity by the Exclusion Principle.—In consequence of the exclusion principle, the multiplicity of terms cannot always attain the maximum which would otherwise be expected from the number of electrons involved. Let us take the case of an atom with six electrons in the L-shell (i.e. $n = 2$). At first sight we should expect that the maximum term multiplicity r would be 7, for if all the six spins were similarly directed we should have $\Sigma = 3$ and therefore $r = 2\Sigma + 1 = 7$. This arrangement of spins, however, cannot occur. Reference to Table XXVI shows that in the L-shell ($n = 2$) only *four* electrons can have similarly directed spins (same sign of m_s). Hence two of the six electrons must necessarily have their spins directed oppositely to the other four. The maximum value of Σ is therefore $(4 \times \frac{1}{2} - 2 \times \frac{1}{2}) = 1$, from which it follows that the maximum term multiplicity is $r = 2\Sigma + 1 = 3$. This is in agreement with observation: the highest term multiplicity is triplet. We easily see that the term multiplicity only rises to the point at which the number of electrons just half fills the group in question. Thereafter, further increase of the number of electrons causes Σ to decrease until the value $\Sigma = 0$ is reached for each completed group and the term multiplicity in the ground state becomes singlet. Thus as a group is gradually filled by addition of successive electrons, the term multiplicity first rises and then falls, the variations being symmetrical with respect to the middle of the group. Hence in the first half of the group we may regard the term multiplicity as depending on the number of places filled by electrons, and in the second half as depending in the same way on the number of places yet to be filled. This is connected also with the inversion of the terms in the second half of a group, i.e. the fact that here the lower terms correspond to higher J-values (p. 330), as in the case of X-ray spectra (p. 295).

The quantum numbers n, l, j, and m may also be used in counting up the number of possible states. In accordance with Table XXIV, p. 322, the same results are obtained, but the sub-groups of the different shells come out differently (compare Table XXIV, p. 322, and Table XXVI, p. 332). Since (jj)-coupling probably holds in the inner shells of atoms, a subdivision of shells of the kind indicated in Table XXIV is to be expected in X-ray spectra. Actually the number of sub-groups in Table XXIV is identical (at least for the innermost shells K, L, M, and N) with the number of absorption edges, i.e. with the number of energy levels as given in fig. 11, p. 296. For a given value of n the number of possible l-values is $n - 1$. The number of possible m_l-values is $2l + 1$ and the number of m_s-values for each combination of n and m_l is 2. Hence the total number of possible states is $\Sigma(4l + 2)$ for all values of l from $l = 0$ to $l = n - 1$. This gives $2n^2$, i.e. 2, 8, 18, 32, &c., for $n = 1, 2, 3, 4$, &c., respectively (compare Table XXIV, p. 322, and Table XXVI, p. 332).

Now the numbers 2, 8, 18, 32 are the numbers of the elements in the various periods of the periodic table (Table I, p. 4). There can be no doubt that in the PAULI exclusion principle we possess the key to the periodic classification of the elements.

D. THE PERIODIC CLASSIFICATION OF THE ELEMENTS

11. The Exclusion Principle and Shell-structure

The shell-structure of atoms, which has already been discussed in Section B (p. 298 *et seq.*), can be accounted for by means of the exclusion principle. The maximum number of electrons with a given principal quantum number, i.e. in a given shell, is restricted in the way shown in Table XXIV (p. 322). If now each element is thought of as built up from the preceding element by the addition of one electron and the simultaneous increase of the nuclear charge by unity, the shells will be successively completed and periods of the lengths 2, 8, 18, 32, &c., may be expected. Actually the first two periods have the expected lengths, but the third has a length of only 8 elements instead of the 18 anticipated. We infer that all the places in the M-shell ($m = 3$) are not filled in the course of the third period; and that the N-shell begins to be formed at potassium, even though ten places are still free in the M-shell. This must be due to the special energy relationships; for the most stable state is always that for which the potential energy is least. In order to follow this out in detail, we shall consider the structure of the periodic table more closely.

In this we shall pursue a train of thought first developed by BOHR. In order to arrive at the structure of an atom, we may start by considering the nucleus with just one electron and determining its ground state (possibly by spectroscopic methods). We may then think of the remaining electrons as added successively (the ground state being determined at each stage), until the neutral atom is finally built up. In the case of Ca ($Z = 20$), for example, it would be necessary, in order to follow out this method, to know the properties of Ca^{19+}. With the means at present at our disposal, however, we cannot get farther than the spark spectra of the 5-fold or 6-fold ionized atom. We are helped out of this difficulty by an empirical fact. Applied to the particular case of Ca, this is, that the structure of 19 of the 20 electrons is the same as the structure of the preceding element. The position taken up by the 20th electron can be easily deduced from the spectral properties of the neutral atom. The fact that the inner electron structure remains unchanged follows, for example, from the rectilinear course of the MOSELEY diagrams of fig. 12 (p. 297), as was pointed out in that connexion. The above procedure is not permissible, however, in all cases. As we see from the changes of slope in the MOSELEY diagrams electrons are sometimes built into inner shells. In the neighbourhood of such places, which have been mentioned previously on p. 306, the above principle of building up the atom must be applied with caution, as we shall see below. Consideration of the higher spark spectra of elements preceding the element in question by several places in the periodic table leads to clear results in such difficult cases.

Period I.—The first member (cf. Table XXVII, p. 336) is *hydrogen*. In accordance with all the facts which have been discussed in detail above, its formula is undoubtedly $H : 1s\,.\,{}^2S_{\frac{1}{2}}$. The hydrogen spectra do not show the splitting which has been discussed in the case of the alkali metals: the hydrogen energy levels are markedly degenerate. The fact that the separations are inappreciable is due to the very small energy of the rotation of the perihelion owing to the mass variability of the electron. The marked degeneracy (e.g. the coincidence of the terms $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$, $3^2S_{\frac{1}{2}}$ and $3^2P_{\frac{1}{2}}$, &c.; also $3^2P_{\frac{3}{2}}$ and $3^2D_{\frac{3}{2}}$) is caused by the fact that the energy change due to electron spin is of exactly the same magnitude as that due to the mass variability of the electron.

The second member of the period is *helium*. As was shown on p. 193, He^+ is certainly analogous to H, the single electron being in a $1s$-orbit. The addition of the second electron must (according to the discussion on p. 285) give rise to a singlet system and a triplet system (see fig. 6, p. 286). The ground state of the term system is a ${}^1S_0$-state. The second electron must therefore also occupy a $1s$-orbit. Hence the formula for the ground state is $He : 1s^2\,.\,1S_0$.

We have seen (p. 331) that the exclusion principle accounts for the fact that there is no term 1^3S_1 corresponding to 1^1S_0. In helium the two places of the K-shell (see Table XXIV, p. 322, $n = 1$) are both filled. The next electron added must necessarily take up an orbit of higher principal quantum number, i.e. it must enter a new shell.

Period II.—The third element is **lithium** ($Z = 3$). The Li^+ spectrum shows the same relative positions of the energy levels as is found for He. Its ground state is therefore $Li^+ : 1s^2\,.\,{}^1S_0$.

What state in the L-shell is occupied by the third electron in neutral Li? The term diagram shows, as for all the alkali metals, that the lowest level is ${}^2S_{\frac{1}{2}}$. Hence the third electron must be bound in a $2s$-state. The ground state of Li may therefore be written $Li : 1s^2\,.\,2s\,.\,{}^2S_{\frac{1}{2}}$.

Beryllium ($Z = 4$). As shown on p. 311, the spectrum of Be^+ corresponds completely to that of Li, except for the displacement of all the energy levels and the consequent displacement of all the spectral lines to shorter wave-lengths owing to the increased nuclear charge. The terms of B^{++} and C^{+++} exhibited in fig. 16, p. 311, also show the same arrangement: in particular the $2^2S_{\frac{1}{2}}$ state is always the lowest. The electronic configuration of Li thus remains unchanged throughout all these elements, and there is no doubt that the arrangement of the first three electrons is the same for all the subsequent elements. The

TABLE XXVII.—ELECTRONIC STRUCTURES AND GROUND TERMS OF THE ELEMENTS

	Shell	K	L		M			N				O			P			Q	
Period	$n =$	1	2		3			4				5			6			7	Ground Term
	$l =$	0	0	1	0	1	2	0	1	2	3	0	1	2	0	1	2	0	
	Element	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	
I.	1 H	1																	${}^2S_{1/2}$
	2 He	2																	${}^1S_0$
II.	3 Li	2	1																${}^2S_{1/2}$
	4 Be	2	2																${}^1S_0$
	5 B	2	2	1															${}^2P_{1/2}$
	6 C	2	2	2															${}^3P_0$
	7 N	2	2	3															${}^4S_{3/2}$
	8 O	2	2	4															${}^3P_2$
	9 F	2	2	5															${}^2P_{3/2}$
	10 Ne	2	2	6															${}^1S_0$
III.	11 Na	2	2	6	1														${}^2S_{1/2}$
	12 Mg	2	2	6	2														${}^1S_0$
	13 Al	2	2	6	2	1													${}^2P_{1/2}$
	14 Si	2	2	6	2	2													${}^3P_0$
	15 P	2	2	6	2	3													${}^4S_{3/2}$
	16 S	2	2	6	2	4													${}^3P_2$
	17 Cl	2	2	6	2	5													${}^2P_{3/2}$
	18 A	2	2	6	2	6													${}^1S_0$
(*a*)	19 K	2	2	6	2	6		1											${}^2S_{1/2}$
	20 Ca	2	2	6	2	6		2											${}^1S_0$
	21 Sc	2	2	6	2	6	1	2											${}^2D_{3/2}$
	22 Ti	2	2	6	2	6	2	2											${}^3F_2$
	23 V	2	2	6	2	6	3	2											${}^4F_{3/2}$
	24 Cr	2	2	6	2	6	5	1											${}^7S_3$
	25 Mn	2	2	6	2	6	5	2											${}^6S_{5/2}$
	26 Fe	2	2	6	2	6	6	2											${}^5D_4$
	27 Co	2	2	6	2	6	7	2											${}^4F_{9/2}$
	28 Ni	2	2	6	2	6	8	2											${}^3F_4$
IV.	— —	—	—		—	—		—	—	—		—	—		—	—		—	— —
(*b*)	29 Cu	2	2	6	2	6	10	1											${}^2S_{1/2}$
	30 Zn	2	2	6	2	6	10	2											${}^1S_0$
	31 Ga	2	2	6	2	6	10	2	1										${}^2P_{1/2}$
	32 Ge	2	2	6	2	6	10	2	2										${}^3P_0$
	33 As	2	2	6	2	6	10	2	3										${}^4S_{3/2}$
	34 Se	2	2	6	2	6	10	2	4										${}^3P_2$
	35 Br	2	2	6	2	6	10	2	5										${}^2P_{3/2}$
	36 Kr	2	2	6	2	6	10	2	6										${}^1S_0$

TABLE XXVII—*Continued*

Period	Shell	K	L		M			N				O			P			Q	Ground Term
	n =	1	2		3			4				5			6			7	
	l =	0	0	1	0	1	2	0	1	2	3	0	1	2	0	1	2	0	
	Element	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	
V. (*a*)	37 Rb	2	2	6	2	6	10	2	6			1							$^2S_{1/2}$
	38 Sr	2	2	6	2	6	10	2	6			2							$^1S_0$
	39 Y	2	2	6	2	6	10	2	6	1		2							$^2D_{3/2}$
	40 Zr	2	2	6	2	6	10	2	6	2		2							$^3F_2$
	41 Cb	2	2	6	2	6	10	2	6	4		1							$^6D_{1/2}$
	42 Mo	2	2	6	2	6	10	2	6	5		1							$^7S_3$
	43 Ma	2	2	6	2	6	10	2	6	6		1							$^6D_{9/2}$
	44 Ru	2	2	6	2	6	10	2	6	7		1							$^5F_5$
	45 Rh	2	2	6	2	6	10	2	6	8		1							$^4F_{9/2}$
	46 Pd	2	2	6	2	6	10	2	6	10									$^1S_0$
(*b*)	47 Ag	2	2	6	2	6	10	2	6	10		1							$^2S_{1/2}$
	48 Cd	2	2	6	2	6	10	2	6	10		2							$^1S_0$
	49 In	2	2	6	2	6	10	2	6	10		2	1						$^2P_{1/2}$
	50 Sn	2	2	6	2	6	10	2	6	10		2	2						$^3P_0$
	51 Sb	2	2	6	2	6	10	2	6	10		2	3						$^4S_{3/2}$
	52 Te	2	2	6	2	6	10	2	6	10		2	4						$^3P_2$
	53 I	2	2	6	2	6	10	2	6	10		2	5						$^2P_{3/2}$
	54 Xe	2	2	6	2	6	10	2	6	10		2	6						$^1S_0$
(*a*)	55 Cs	2	2	6	2	6	10	2	6	10		2	6		1				$^2S_{1/2}$
	56 Ba	2	2	6	2	6	10	2	6	10		2	6		2				$^1S_0$
	57 La	2	2	6	2	6	10	2	6	10		2	6	1	2				$^2D_{3/2}$
(Rare earths)	58 Ce	2	2	6	2	6	10	2	6	10	1	2	6	1	2				$^3H_4$
	59 Pr	2	2	6	2	6	10	2	6	10	2	2	6	1	2				$^4K_{11/2}$
	60 Nd	2	2	6	2	6	10	2	6	10	3	2	6	1	2				$^5L_6$
	61 Il	2	2	6	2	6	10	2	6	10	4	2	6	1	2				$^6L_{9/2}$
	62 Sm	2	2	6	2	6	10	2	6	10	5	2	6	1	2				$^7K_4$
	63 Eu	2	2	6	2	6	10	2	6	10	6	2	6	1	2				$^8H_{3/2}$
	64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	2				$^9D_2$
	65 Tb	2	2	6	2	6	10	2	6	10	8	2	6	1	2				$^8H_{17/2}$
	66 Dy	2	2	6	2	6	10	2	6	10	9	2	6	1	2				$^7K_{10}$
	67 Ho	2	2	6	2	6	10	2	6	10	10	2	6	1	2				$^6L_{19/2}$
	68 Er	2	2	6	2	6	10	2	6	10	11	2	6	1	2				$^5L_{10}$
	69 Tm	2	2	6	2	6	10	2	6	10	12	2	6	1	2				$^4K_{17/2}$
	70 Yb	2	2	6	2	6	10	2	6	10	13	2	6	1	2				$^3H_6$
	71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	2				$^2D_{3/2}$

TABLE XXVII—*Continued*

	Shell	K	L		M			N				O			P			Q	
	$n =$	1	2		3			4				5			6			7	
Period	$l =$	0	0	1	0	1	2	0	1	2	3	0	1	2	0	1	2	0	Ground Term
	Element	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	*d*	*f*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	
VI.	72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	2				$^3F_2$
	73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2				$^4F_{3/2}$
	74 W	2	2	6	2	6	10	2	6	10	14	2	6	4	2				$^5D_0$
(*a*)	75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5	2				$^6S_{5/2}$
	76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6	2				$^5D_4$
	77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7	2				$^4F_{9/2}$
	78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	1				$^3D_3$
	79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1				$^2S_{1/2}$
	80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2				$^1S_0$
	81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1			$^2P_{1/2}$
(*b*)	82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2			$^3P_0$
	83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3			$^4S_{3/2}$
	84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4			$^3P_2$
	85 —	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5			$^2P_{3/2}$
	86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6			$^1S_0$
	87 —	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		1	$^2S_{1/2}$
	88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		2	$^1S_0$
VII.	89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2	$^2D_{3/2}$
	90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2	$^3F_2$
	91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	3	2	$^4F_{3/2}$
	92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	5	1	^7S

addition of a fourth electron to Be^+ gives neutral Be. Its spectrum can be ordered so as to give a singlet and a triplet system, in accordance with the possible orientations of the spins of the two outer electrons. In contrast to He, terms also occur which correspond to *simultaneous* excitation of both valency electrons.

The ground state is a $^1S_0$-state. This is in agreement with the expected entry of the fourth electron into a 2*s*-state. The allocation is unique, in view of the fact that the corresponding triplet term 2^3S_1 does not occur, being excluded for the same reason as that mentioned in connexion with He.

Boron (Z = 5). As is proved by the ground term of the B spectrum, the fifth electron takes up a 2*p*-orbit. The formula is therefore

$$B : 1s^2 \,.\, 2s^2 \,.\, 2p \,.\, {}^2P_{\frac{1}{2}}.$$

We here have a P-term instead of an S-term as ground state. (We have previously met with the same thing in the case of aluminium (fig. 7, p. 288), another trivalent element.) The reason in the present case is that the $2p$-electron, which is the most loosely bound, can at most return to the $2p$-state after excitation, because both the $2s$-states are already occupied. The lowest available s-state is the $3s$-state, so that the S-series begin with $n = 3$.

The filling up of the possible p-states takes place progressively up to *neon* ($Z = 10$), at which element the L-shell is completely filled with 8 L-electrons. The whole shell has zero resultant angular momentum. This may be seen from Table XXVI, p. 332, by considering the possible vector orientations. It also follows from the spectrum, the lowest term of which is a $^1S_0$-term in accordance with the arrangement Ne : $1s^2 . 2s^2 . 2p^6$.

Period III.—In this period the M-shell is built up in exactly the same way as the L-shell in Period II. At A ($Z = 18$) the sub-group $3p$ is completed, the ground term having the formula

$$\mathrm{A} : 1s^2 . 2s^2 . 2p^6 . 3s^2 . 3p^6 . {}^1S_0.$$

12. The Higher Periods

Period IV.—If the process of shell-filling continued in a regular manner, the third period would go on after argon until the ten $3d$-states of the M-shell were filled. Instead of this an alkali metal, *potassium*, appears as the 19th element—an atom which, as is discussed in detail above, has an S-state as ground state. The last added electron must therefore be an s-electron: it must occupy a $4s$-state. This state must evidently be of lower energy than a $3d$-state. In other words, a certain excitation energy must be expended in order to raise the electron from the $4s$-orbit into the $3d$-orbit. Hence we must expect that in the spectrum of K the $3d$-terms will lie above the $4s$-terms. As fig. 22 shows, this is in fact the case.

The reason for this behaviour is not difficult to grasp. In the BOHR model a $3d$-orbit is circular (p. 199), whereas a $4s$-orbit is a very eccentric ellipse which penetrates into the atomic core. Hence it may well happen that the $4s$-orbit, in which the electron (at least for a small part of the orbit) is under the influence of a relatively large effective nuclear charge, may represent a state of lower energy than the $3d$-orbit, in which the electron never comes near the nucleus and is throughout under the influence of a screened nuclear charge of effective value unity.

Consideration of the term diagram of Al ($Z = 13$)—see fig. 7, p. 288—shows that the $3d$-states lie higher than the $4s$-states even for this atom. (Here, of course, this does not lead to any complication as far as the ground state is concerned, because the $3p$-states of very low energy are still unoccupied.) It is therefore quite intelligible, and indeed what we may expect in the light of the discussion of the spectra, that when it comes to a choice between 4*s*- and 3*d*-states, the former will have the lower energy and will be taken up in the ground state.

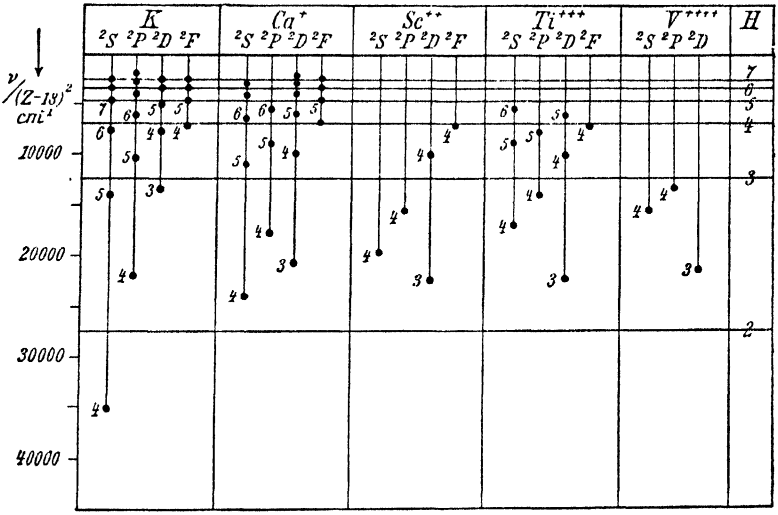


Fig. 22.—Binding of the 19th electron for nuclear charges of 19 to 22

At this point it becomes questionable whether the configuration of the K atom should be assumed for the ion Ca⁺ of the next element, *calcium* (Z = 20); for the increase in the nuclear charge will cause a shrinking of the orbits, and it is not possible to say at once which state will have the lowest energy. However, the spectrum of Ca⁺ (fig. 22) shows that here again the 4*s*-state is the lowest. The 20th electron is likewise bound in a 4*s*-orbit, as is to be expected from the analogy between the chemical properties of Ca and those of Mg, and as follows from the term diagram, which has a $^1S_0$-term as lowest term.

Now what happens to the structure as we pass on to the next element, *scandium* (Z = 21)? Comparison of the spectrum of Ca⁺ with that of K (fig. 22) shows that the 4*s*-state has already moved very close to the 3*d*-state. To make sure, therefore, we make a further comparison with the spectrum of Sc⁺⁺. As fig. 22 shows, the lowest term is found to be a 3*d*-term. Thus in Sc⁺⁺ the 19th electron is no longer (as in K) in a 4*s*-orbit, but in a 3*d*-orbit, the position to be expected in a normal progressive filling of the M-shell. This holds also for the succeeding elements (see fig. 22), so that from scandium onwards we must allot the 19th electron to a 3*d*-state. What state, then, does the 20th electron of scandium take up? Information on this point can be derived from the spectrum of Sc^+. Here experiment shows that the ground term is a ^{3}D-term, as is to be expected from the structure $Sc^+ : (Ne) . 3s^2 . 3p^6 . 3d . 4s . {}^3D$. Thus the 20th electron takes up a $4s$-orbit. What state is taken up by the 21st electron of scandium? The ground terms to be expected for the different conceivable states of this electron may be worked out. For example, if the 21st electron were to take up a $3d$-orbit, the ground state would be a ^{4}F-term; if the orbit taken up were a $4s$-orbit, a ^{2}D-term would result, and so on. Experiment shows that the lowest term is in fact a ^{2}D-term. It follows that the ground state of scandium is

$$Sc : (Ne) . 3s^2 . 3p^6 . 3d . 4s^2 . {}^2D.$$

The considerations given above for the 19th to the 21st electrons may be extended throughout the periodic table. In this way, making use of arc and spark spectra and also of the clues to irregularities of structure furnished by the MOSELEY diagrams, it is possible to determine the electronic configuration for all the elements. A degree of uncertainty remains in some cases. For example, we do not know precisely how the electrons are distributed between the O- and P-shells in the ground state of the rare-earth atoms ($Z = 57$ to 71). Our knowledge of the shell-structure of the elements in the ground states is summarized in Table XXVII (p. 336).

The structure of the periods may be briefly discussed in the light of this table. The process of filling up the M-shell, which according to Table XXIV, p. 322 can have 10 electrons in $3d$-states, is not completed until Cu ($Z = 29$). This is the first element to have a completely filled M-shell. It has, in addition, a single electron in the N-shell, and this is the reason why copper may be univalent. Very near to this ground state, however, is a state with the configuration $(A) . 3d^9 . 4s^2 . {}^2D$, in which there are two electrons in the N-shell. The energy difference between these two states is only 0·15 electron-volt ($= 1200$ cm.$^{-1}$). Hence this state also occurs in chemical reactions and copper may be divalent.

We see that Ni, which has just the ten electrons necessary to fill the d-states of the M-shell and so complete the shell, is not in fact an inert gas, because two of the electrons occupy $4s$-states, in which they are more tightly bound than they would be in the two missing $3d$-states. After Cu the N-shell continues for a time to be built up in a regular fashion, the elements showing characteristic chemical properties similar to those of the corresponding elements in the preceding periods.

Period V.—At Rb ($Z = 37$) the building up of the O-shell ($n = 5$) commences, in spite of the fact that the $4d$- and $4f$-states are not yet occupied. Thus here we encounter conditions which are quite similar to those already discussed for the elements K to Sc. Here again it is at a trivalent element, Y ($Z = 39$), that the $5s$- and the $4d$-states become practically equal in energy. This gives rise to the possibility of different configurations with only slightly differing energies. Hence small energy changes, in some cases even violent thermal agitation, can give rise to excited states not far removed from the ground state. The elements therefore exhibit a great variety of chemical properties and possess a number of different valencies. The 4*d*-group is completed at Pd (Z = 46). This element has the character of an inert gas in so far as its atoms contain only completed sub-groups. Its ground term is also $^1S_0$. This is in accord with its marked chemical inertness. The fact that Pd is not an inert gas is explained as follows. In contrast to the real inert gases, for which the first excited state lies very high above the ground state (see Table XXII, p. 301), Pd has energy levels lying quite close to the ground state. Amongst such states are those with the configurations (Kr) . $4d^9 . 5s$ and $4d^8 . 5s^2$, &c. Since these states are excited to an appreciable extent by thermal agitation, a certain chemical reactivity results and the inert-gas character is only feebly exhibited.

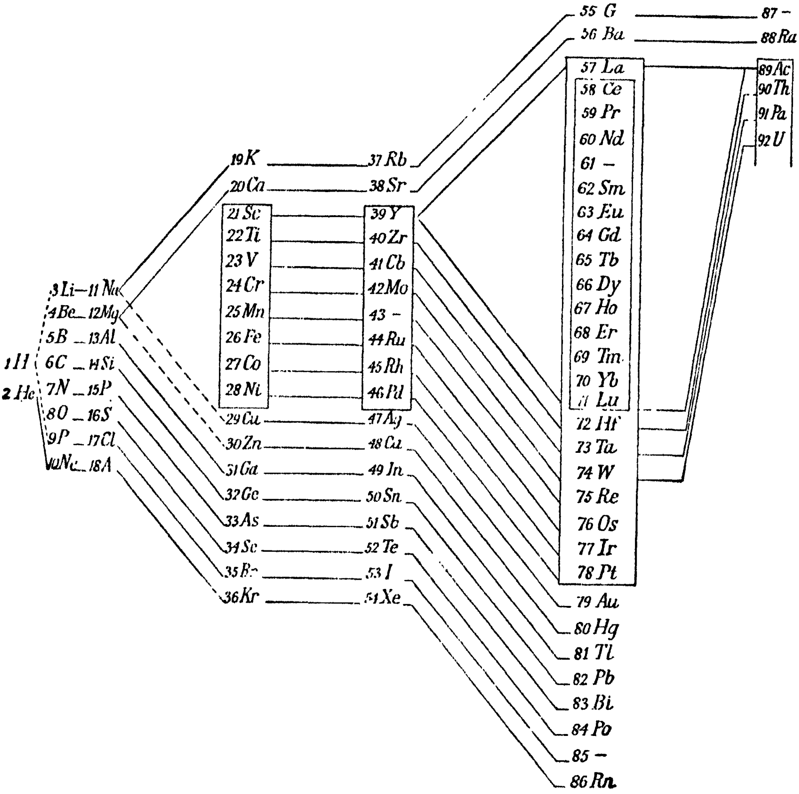
From Ag (Z = 47) onwards the regular filling of the O-shell proceeds, and we again obtain a series of elements with well-defined valencies and marked chemical similarity to those of Series II, III, and IV (Cu to Kr). The filling of the 5*s*- and 5*p*-groups is completed at the inert gas Xe (Z = 54).

Period VI.—The 6*s*-orbits are so eccentric, and consequently penetrate so deeply into the atomic core, that they now represent closer binding than the circular 4*f*-orbits. Although 4*f*-states are still unoccupied (and likewise 5*f*- and 5*g*-states), the 55th electron takes up a 6*s*-state in Cs (Z = 55), thus conferring upon this element the character of an alkali metal. Then, just as for Sc, the competition of the 5*d*-states makes itself felt in the trivalent element La (Z = 57). But before any more of these states can be filled, the 4*f*-states begin to be filled (of which the maximum possible number is 14 (see Table XXVI, p. 332)). This may be concluded from spectroscopic evidence of the same kind as that given in fig. 22, p. 340 for the 19th electron. The 4*f*-states are successively filled without interruption in the series of 14 elements (the so-called rare earths) from cerium to lutecium (Z = 58 to 71). Since the configuration of the outer electrons is the same (or practically the same) for all these 14 elements, they exhibit a very remarkable similarity in their chemical and physical properties.

According to the exclusion principle, 14 is the maximum number of 4*f*-electrons. Hence the next electron added to form Hf (Z = 72) must take up a position nearer the outside of the atom. This element hafnium therefore cannot belong to the rare earths, but rather must bear a resemblance to Zr (Z = 40).

At the time when Bohr first developed the ideas which form the basis of the above treatment, i.e. in 1922, when the exclusion principle was not yet known, the element 72 had not been discovered. Up to that time it had been sought for amongst the rare earths. BOHR predicted that it should on the contrary resemble zirconium and ought therefore to be sought for in minerals containing this element. In the light of this prediction, the element 72 was actually discovered in the same year by PANETH and HEVESY. In honour of BOHR's birthplace, Copenhagen, it was given the name *hafnium.** It occurs mixed with zirconium in surprisingly large proportions, and most zirconium preparations contain appreciable quantities of hafnium.

TABLE XXVIII.—DIAGRAM OF THE PERIODIC SYSTEM ACCORDING TO BOHR



At Pt (Z = 78), whose outer electronic configuration is similar to that of Ni, the number of electrons necessary to fill the $5d$-states completely is reached, though one of the electrons actually takes a $6s$-state. Then from Au (Z = 79) onwards the $6s$- and $6p$-states are regularly filled, in spite of the fact that the $5f$- and $5g$-states remain

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* From *Hafnia*, the old Latin name for Copenhagen.

TABLE XXIX.—PERIODIC TABLE

I.	1 H s ^{2}S	2 He s^2 ^{1}S							
II.	3 Li s ^{2}S	4 Be s^2 ^{1}S							
III.	11 Na s ^{2}S	12 Mg s^2 ^{1}S							
IV.	19 K s ^{2}S	20 Ca s^2 ^{1}S	21 Sc ds^2 ^{2}D	22 Ti d^2s^2 ^{3}F	23 V d^3s^2 ^{4}F	24 Cr d^5s ^{7}S	25 Mn d^5s^2 ^{6}S	26 Fe d^6s^2 ^{5}D	27 Co d^7s^2 ^{4}F
V.	37 Rb s ^{2}S	38 Sr s^2 ^{1}S	39 Y ds^3 ^{2}D	40 Zr d^2s^2 ^{3}F	41 Cb d^4s ^{6}D	42 Mo d^5s ^{7}S	43 Ma (d^6s) ^{6}D	44 Ru d^7s ^{5}F	45 Rh d^8s ^{4}F
VI.	55 Cs s ^{2}S	56 Ba s^2 ^{1}S	57 La f^0ds^2 ^{2}D	72 Hf $f^{14}d^2s^2$ ^{3}F	73 Ta (d^3s^2) ^{4}F	74 W d^4s^2 ^{5}D	75 Re (d^5s^2) ^{6}S	76 Os (d^6s^2) ^{5}D	77 Ir (d^7s^2) ^{4}F
VII.	87 — s ^{2}S	88 Ra s^2 ^{1}S	89 Ac (ds^2) ^{2}D	90 Th (d^2s^2) ^{3}F	91 Pa (d^3s^2) ^{4}F	92 U (d^5s) ^{7}S			
			58 Ce f^1ds^2 ^{3}H	59 Pr f^2ds^2 ^{4}K	60 Nd f^3ds^2 ^{5}L	61 Il f^4ds^2 ^{6}L	62 Sm f^5ds^2 ^{7}K	63 Eu f^6ds^2 ^{9}H	64 Gd f^7ds^2 ^{9}D

unoccupied. At radon (Z = 86) the 6*s*- and 6*p*-states are completely filled and we have an inert gas. The next element (Z = 87) is unknown. Here the filling of the Q-shell (*n* = 7) commences, so that it must be an alkali metal. The element Ra (Z = 88) is known and is of typical alkaline-earth character, both chemically and spectroscopically. The periodic table comes to an end with uranium (Z = 92), nuclei of higher charge being no longer stable. The chemical properties of elements beyond uranium can likewise be derived from considerations like those given above, so that it is not impossible that such elements (if indeed they can exist at all) may one day be isolated, perhaps from cosmic material.

Relationships between the Elements.—As may be seen from Table XXVII, p. 336, chemical similarities between different elements are mainly due to similarities in the configuration of the outer electrons of the atoms. Thus all the alkali metals have a single outer *s*-electron, all the alkaline-earth metals have two such

WITH STATES OF VALENCY ELECTRONS

										I.
			5 B s^2p ^2P	6 C s^2p^2 ^3P	7 N s^2p^3 ^4S	8 O s^2p^4 ^3P	9 F s^2p^5 ^2P	10 Ne s^2p^6 ^1S	II.
			13 Al s^2p ^2P	14 Si s^2p^2 ^3P	15 P s^2p^3 ^4S	16 S s^2p^4 ^3P	17 Cl s^2p^5 ^2P	18 A s^2p^6 ^1S	III.
28 Ni d^8s^2 ^3F	29 Cu $d^{10}s$ ^2S	30 Zn $d^{10}s^2$ ^1S	31 Ga s^2p ^2P	32 Ge s^2p^2 ^3P	33 As s^2p^2 ^4S	34 Se s^2p^4 ^3P	35 Br s^2p^5 ^2P	36 Kr s^2p^6 ^1S	IV.
46 Pd d^{10} ^1S	47 Ag $d^{10}s$ ^2S	48 Cd $d^{10}s^2$ ^1S	49 In s^2p ^2P	50 Sn s^2p^2 ^3P	51 Sb s^2p^3 ^4S	52 Te s^2p^4 ^3P	53 I s^2p^5 ^2P	54 Xe s^2p^6 ^1S	V.
78 Pt d^9s ^3D	79 Au $d^{10}s$ ^2S	80 Hg $d^{10}s^2$ ^1S	81 Tl s^2p ^2P	82 Pb s^2p^2 ^3P	83 Bi s^2p^3 ^4S	84 Po s^2p^4 ^3P	85 — s^2p^5 ^2P	86 Rn s^2p^6 ^1S	VI.
										VII.
65 Tb f^8ds^2 ^8H	66 Dy f^9ds^2 ^7K	67 Ho $f^{10}ds^2$ ^6L	68 Er $f^{11}ds^2$ ^5L	69 Tm $f^{12}ds^2$ ^4K	70 Yb $f^{13}ds^2$ ^3H	71 Lu $f^{14}ds^2$ ^2D				

electrons ($s^2 . {}^1S$), all halogens have two *s*- and five *p*-electrons ($s^2 . p^5 . {}^2P$), &c.

The elements of the sub-groups of the periodic table are characterized by outer *d*-electrons. For instance, in group III the main group elements B and Al, as well as Ga, In, and Tl, all possess the arrangement s^2p in the outermost shell, whereas the sub-group elements Sc, Y, La, and Ac all have s^2d. Analogous relationships are found in group IV. The extent to which the periodicity of chemical properties, especially of valency, depends on the periodicity of atomic structure treated above will be discussed in Chapter VI, p. 361 *et seq.* In Table XXVIII another way of representing the relationships of the chemical elements is reproduced. This form of the periodic system is due to JULIUS THOMSEN and BOHR. A further table is also given (Table XXIX) in which the elements are arranged in long periods and the configuration of the electrons to which the characteristic chemical properties are due is given for each element.

13. Magnetic Properties

Mention has been made above of several physical properties whose periodic variation with atomic number indicates that they are related to atomic structure. The periodicity of chemical properties will be discussed later (p. 383). In the present section we shall consider certain physical properties which can be treated quantitatively in the light of what has been said about atomic structure above.

Foremost amongst such properties are the magnetic properties. We have already seen on p. 317 that every alkali-like atom behaves like a circulatory electric charge with the magnetic moment $\mathrm{M} = jg\mu_0$ or more exactly (see p. 312) $\mathrm{M} = \sqrt{j(j+1)}g\mu_0$. The quantities g and μ_0 in these formulæ are given respectively by

$$g = \frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

and

$$\mu_0 = \frac{eh}{4\pi mc},$$

where m is the mass of an electron. Exactly analogous formulæ also hold for atoms with more than one valency electron, the quantum numbers Σ, L, and J being substituted respectively for s, l, and j. Hence if the nature of the ground state is known, we have all the quantities necessary for the calculation of g and consequently of the magnetic moment M of the atom. The experimentally observable quantity is the magnetic susceptibility K of the element, which according to Vol. III, p. 448, is given by

$$\mathrm{K} = \frac{n\mathrm{M}^2}{3k\mathrm{T}},$$

where n is the number of atoms per c.c. Thus the magnetic moment of the atom can be calculated from experimentally determined susceptibilities. In comparing such experimental values with those to be expected theoretically, a correction must be applied if all the atoms are not (as assumed above) in the ground state. Such a correction will obviously be necessary in cases where the atom possesses energy levels so near the ground state as to be appreciably excited by thermal agitation under the conditions of experiment. If $\Delta\mathrm{W}$ is the energy difference between the ground state and such a level, the number of excited atoms will be proportional to $e^{-\Delta\mathrm{W}/k\mathrm{T}}$. Hence, knowing the nature of the excited state, we can make due allowance for its contribution to the mean magnetic moment of the atoms. The comparison of experimental and theoretical values also involves the assumption that neighbouring atoms do not appreciably affect one another. This last assumption is best justified for gases. In the case of sodium vapour

GERLACH has found a value for the susceptibility which is in very good agreement with that derived from the theory given above. Another case in which there is little mutual disturbance between neighbouring systems is that of the trivalent ions of the rare-earth metals. These ions differ from the corresponding neutral atoms in having lost the *5d*- and *6s*-electrons. As we see from Table XXVII, p. 336, the *4s*-, *4p*-, *4d*-, *5s*-, and *5p*-sub-groups are complete, so that the nature of the ground term is determined solely by the *4f*-electrons. The theoretical ground states (p. 330) are shown in Table XXX, in which the letters H and I stand for L = 5 and L = 6 respectively. Some of the values of L and J are found to be very large, so that very strong paramagnetic properties are to be anticipated from the theory. Actually the ions in question have long been known to show strong paramagnetic behaviour. In Table XXX, under the heading M_0/μ_0, are given the values of the magnetic moments of the ions (with μ_0 as unit), calculated from the given ground terms.

TABLE XXX.—MAGNETIC MOMENTS OF THE IONS OF THE RARE-EARTH ELEMENTS

Ion	*4f*-electrons	Ground term	$\frac{M_0}{\mu_0}$	$\frac{M}{\mu_0}$
La^{+++}	0	$^1S_0$	0·00	0·00
Ce^{+++}	1	$^2F_{5/2}$	2·54	2·5
Pr^{+++}	2	$^3H_4$	3·58	3·6
Nd^{+++}	3	$^4I_{9/2}$	3·62	3·6
Il^{+++}	4	$^5I_4$	2·68	2·8
Sm^{+++}	5	$^6H_{5/2}$	0·84	1·7
Eu^{+++}	6	$^7F_0$	0·00	3·5
Gd^{+++}	7	$^8S_{7/2}$	7·9	7·9
Tb^{+++}	8	$^7F_6$	9·7	9·7
Dy^{+++}	9	$^6H_{15/2}$	10·6	10·6
Ho^{+++}	10	$^5I_8$	10·6	10·6
Er^{+++}	11	$^4I_{15/2}$	9·6	9·6
Tm^{+++}	12	$^3H_6$	7·5	7·5
Yb^{+++}	13	$^2F_{7/2}$	4·5	4·5
Lu^{+++}	14	$^1S_0$	0·00	0·00

When proper account is taken of the energy levels lying close to the ground level (due to the term multiplicities, i.e. the various J-values), the values given under the heading M/μ_0 are obtained. These are the values to be expected from measurements carried out at room temperature. As is seen from the table, the correction to be applied on account of the excited states is small, except for Sm and Eu. Fig. 23 shows graphically the comparison between these theoretical values and the values actually obtained by experiment. The limits of error on the latter are indicated by the short vertical lines. The small circles represent the theoretical values. For clearness they are joined by a continuous curve. We see that the peculiar form of this curve is excellently accounted for by the theory.

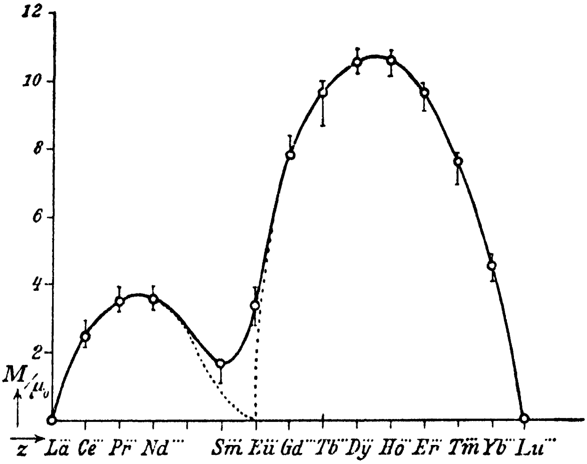

Fig. 23.—Magnetic moments of the ions of the rare earth metals in the solid and liquid states. (The dotted curve is that obtained when no account is taken of excited states.)

A further important contribution from the experimental side has been made by Sucksmith. As was mentioned briefly on p. 446 of Vol. III, he measured the mechanical couple which acts on a suspended paramagnetic substance when a magnetic field is suddenly applied to it. This effect may be regarded as due to the Larmor precession of the atomic " magnetic top " under the influence of the applied field (see Vol. III, *loc. cit.*). The ratio of mechanical angular momentum to magnetic moment is given by $G = 2mc/(ge)$, where g has the value given above. Sucksmith not only succeeded in demonstrating the existence of the very small effect for the salts of the rare earths, but was also able to measure it very exactly. In the case of Dy, for example, his measurements give $g = 1{\cdot}28$, as compared with the value 1·33 calculated from the electronic configuration of the ion.

The Ions of Period IV (Ca^{++} to Zn^{++}).—Very poor agreement with experiment is obtained if the magnetic properties of the ions Ca^{++} to Zn^{++} are calculated by the above method, and only the ground states are taken into account. In fig. 24 (as in the preceding figure) the experimental values are plotted as vertical lines, while the theoretical values lie on the dotted curve. Better agreement is obtained when the excited states are taken into account. The continuous curve represents the theoretical results when full allowance is made for the energy levels in the neighbourhood of the ground level, and therefore refers to high temperatures, when all these levels are appreciably excited. The observed values might be expected to lie between the two curves, but this is not true for all the ions. The discrepancies are probably due in part to displacements of the energy levels (a kind of PASCHEN-BACK effect) occasioned by the strong interactions of the fields of ions approaching close to one another as a result of thermal agitation.

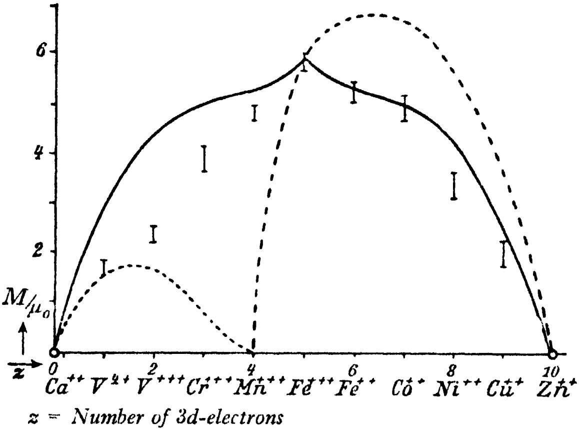

Fig. 24.—Magnetic moments of the ions of Period IV, Ca to Zn, in the solid and liquid states

Diamagnetic Atoms.—All atoms and ions for which the total angular momentum is zero (i.e. $J = 0$) in the ground state possess no magnetic moment, and hence exhibit diamagnetic properties only. To this class belong all systems whose electronic configuration contains completed groups only, and in particular those with inert-gas structure. The following atoms and ions are actually found to be diamagnetic: He, Li^+, Be^{++}, B^{+++}, O^{--}, F^-, Ne, Na^+, Mg^{++}, Al^{+++}, S^{--}, Cl^-, A, K^+, Ca^{++}, Sc^{+++}, Ti^{++++}; also Cu^+, Zn^{++}, and Ga^{+++}, these latter on account of the configuration $3d^{10}$ (see Table XXVII, p. 336).

Effect of Energy Levels near the Ground State on the Specific Heat.—When an atom or ion possesses energy levels lying close above the ground level, a relatively small amount of energy suffices to make the system assume an excited state. Since the number of atoms with an energy ΔW greater than the energy of the ground state is $e^{-\frac{\Delta W}{kT}}$ and therefore increases with the temperature, the result must be an "anomalous" variation of specific heat with temperature; for a fraction of the thermal agitation is transformed into internal energy of the atoms (appearance of new degrees of freedom). Effects of this kind appear to have been actually observed, particularly for salts of the rare-earth metals.

E. THE INFLUENCE OF THE NUCLEUS ON ATOMIC SPECTRA

14. Hyperfine Structure

Experimental results of various kinds (to be discussed below) indicate that the proton must be regarded as having a spin like the electron, the mechanical angular momentum being again of the order of $h/(2\pi)$—actually an integral multiple of $\frac{1}{2}h/(2\pi)$. Since, however, the mass of the proton is about 2000 times that of the electron, the magnetic moment of the proton is presumably only $\frac{1}{2000}$ of that of the electron (see the equation on p. 208). More complicated nuclei must also be regarded as having spins.

The first piece of evidence for definite nuclear spins is the observed fine structure (so-called *hyperfine structure*) of each of the components of the multiplet fine structure of atomic terms discussed above. As we have seen, the multiplet fine structure is explained as being due to the spin of the electron. No further cause for a splitting of energy levels is to be found in the extra-nuclear electronic structure of the atom, and hence we are led to the conclusion that the observed hyperfine structure must be a nuclear effect. This conclusion is supported (see below) by certain peculiarities of band spectra, by determinations of electric moments by the molecular-beam method, and also by the discovery of two modifications of the hydrogen molecule.

Nuclear spin is not the only nuclear property which may produce a hyperfine structure of the multiplet levels. In the first place it must be remembered that elements exist as mixtures of isotopes of different nuclear masses. Since the RYDBERG constant R depends on the nuclear mass, slightly different energy levels will result. Conversely, the observed fine structure could be used for the detection of isotopes. Thus in 1932 UREY actually succeeded in showing that the spectrum of hydrogen contains, in addition to the ordinary lines of the Balmer series, other lines ascribable to a hydrogen atom with nuclear mass 2. This resulted in the discovery of the so-called heavy hydrogen isotope (p. 96). The effect of different isotopic nuclei can also be detected in other spectra, e.g. in that of Cd, though here the cause is probably differences of electrical properties rather than differences of mass.

Hyperfine structures, however, have been observed even for elements (e.g. bismuth) which have only *one* isotope. Here there can be no doubt that the cause is the electrical properties of the nucleus. Moreover, the appearance of sharp lines and the discovery of whole-number relationships between the energy differences of the levels necessarily lead to the idea of sharply-defined (i.e., in the usual language of atomic structure, quantized) nuclear states. BACK has actually succeeded in demonstrating the ZEEMAN splitting of the hyperfine structure components. The observed phenomena can be very well accounted for by ascribing to the nucleus an angular momentum vector **I** and a corresponding quantum number i. This vector **I** combines with the angular momentum vector **J** to give a resultant **F**. Fig. 25 gives an example of hyperfine structure. Since the magnetic moment of the nuclear spin of a nucleus of mass M is only m/M times that of an electron (mass m), the separation of the hyperfine structure components of a line is correspondingly small in comparison with the separation of the ordinary multiplet components. Thus for Bi the ratio of the separations may be expected to be only about 1 : 40,000. This is in good agreement with observation, as far as order of magnitude is concerned. Here the multiplet separation is of the order of 15,000 cm.$^{-1}$, while the hyperfine separation is only about 0·1 to 0·5 cm.$^{-1}$. On account of the smallness of the effect, investigations of hyperfine structure are always carried out with atoms of high mass (like Bi); for only in such cases can the broadening of the lines by the Doppler effect be kept sufficiently small without raising serious experimental difficulties.

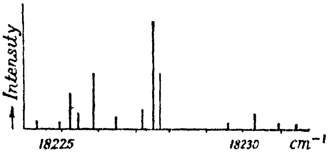

Fig. 25.—Observed hyperfine structure of the line 5485 Å. of Li II

Table XXXI gives the nuclear angular momenta (expressed as the quantum number i and called *nuclear moments*) which have so far been obtained from hyperfine structure and other measurements.

TABLE XXXI.—NUCLEAR MOMENTS (i)

Element	i	Element	i	Element	i
H^1	$\frac{1}{2}$	Mn^{55}	$\frac{5}{2}$	$Ba^{136, 138}$	0
He^4	0	$Cu^{63, 65}$	$\frac{3}{2}$	La^{139}	$\frac{5}{2}$
Li^6	0	$Ga^{69, 71}$	$\frac{3}{2}$	Pr^{141}	$\frac{5}{2}$
Li^7	$\frac{3}{2}$	As^{75}	$\frac{3}{2}$	$Re^{187, 189}$	$\frac{5}{2}$
C^{12}	0	$Br^{79, 81}$	$\frac{3}{2}$	Au^{197}	$\frac{3}{2}$?
N^{14}	1	Rb^{85}	$\frac{3}{2}$?	Hg^{199}	$\frac{1}{2}$
O^{16}	0	$Cd^{111, 113}$	$\frac{1}{2}$	Hg^{201}	$\frac{3}{2}$
F^{19}	$\frac{1}{2}$	$Cd^{110, 112, 114, 116}$	0	$Hg^{198, 200, 202, 204}$	0
Na^{23}	$\frac{5}{2}$?	In^{115}	$\frac{9}{2}$	$Tl^{203, 205}$	$\frac{1}{2}$
P^{31}	$\frac{1}{2}$	$Sb^{121, 123}$	$\frac{5}{2}$?	Pb^{207}	$\frac{1}{2}$
S^{32}	0	I^{127}	$\frac{9}{2}$	$Pb^{204, 206, 208}$	0
Cl^{35}	$\frac{5}{2}$	Cs^{133}	$\frac{7}{2}$?	Bi^{209}	$\frac{9}{2}$
K^{39}	$>\frac{1}{2}$?	Ba^{137}	$\frac{3}{2}$?		

Considerable uncertainty still attaches to some of the data, owing to the difficulty of determining the very small frequency differences involved. Interferometric methods are generally used. Since the spins of the proton and electron are probably equal, namely $\frac{1}{2}h/(2\pi)$, atoms with even nuclear charges may be expected to have nuclear moments which are even multiples of $\frac{1}{2}h/(2\pi)$, while atoms with odd nuclear charges may be expected to have nuclear moments which are odd multiples of $\frac{1}{2}h/(2\pi)$. As may be seen from Table XXXI, this is *not* the case. This raises difficulties which have so far not been overcome, and shows that we still have no satisfactory theory of nuclear structure. (See the sections on the neutron, p. 111, and β-ray energy, p. 20.)

Para- and Ortho-Hydrogen.—In diatomic molecules with similar nuclei the existence of nuclear spin gives rise to an effect similar to that occurring with electrons (pp. 274, 388). In fact there must be an energy difference between corresponding configurations with parallel and antiparallel nuclear spins, rather like that observed in the analogous case of atoms with two electrons (e.g. helium: ortho-helium and parhelium). It has in fact been found that the hydrogen molecule H_2 exists in two different modifications called *para-hydrogen* and *ortho-hydrogen*. On account of the different energy states of rotation (see below), the two modifications differ from one another in specific heat. If ordinary hydrogen H_2 is absorbed by wood charcoal at about 20° Abs., it is almost completely transformed within a few hours into para-hydrogen. As will be explained in more detail later, we may conclude from the variation of the specific heats with temperature that in para-hydrogen the two nuclei must have oppositely-directed spins, while in ortho-hydrogen the two spins must be similarly directed. Ortho-hydrogen cannot be prepared in a pure state, because its energy content at low temperatures is always greater than that of para-hydrogen. Under ordinary conditions hydrogen is a mixture of the two forms in the ratio 3 : 1. This is the proportion which is spontaneously assumed at high temperatures. As we shall see later, spectroscopic data also lead to the same conclusion.

So far it has not been found possible to detect differing modifications of an analogous nature in the case of other molecules with similar nuclei (e.g. N_2 or the halogens, for which such modifications are to be expected theoretically).

Influence on the Rotational States.—The wave-mechanical calculations show that the nuclear moments must have an influence on the rotational states of molecules. A certain extension of the exclusion principle is thereby obtained. For a diatomic molecule with zero total electronic angular momentum the theory states that when the two nuclear spins are parallel, only those rotational states with odd rotational quantum numbers are possible. On the other hand, if the nuclear spins are antiparallel, the molecule in the ground state can only assume those rotational states which have even rotational quantum numbers (see pp. 380 and 382).

F. SOME DEDUCTIONS FROM WAVE-MECHANICAL THEORY

15. The Principle of Indeterminacy

Electromagnetic phenomena in relatively large regions of space and, so far as oscillations are concerned, at low frequencies are satisfactorily accounted for by MAXWELL'S equations, i.e. on the basis of a continuum theory. Within the atom, on the other hand, we have seen in this volume that other laws hold. The most remarkable feature of these atomic laws is their discontinuity, which is manifested most clearly by the sharp lines of atomic spectra. This discontinuity is characterized by the appearance of the quantum of action h in the formulæ. Thus it appears that the substratum of electromagnetic processes has not the nature of a continuum, but must have a discontinuous structure which is measured by the constant h. At present we have no means of elucidating this structure. Hence it is clear that, for the time being at least, we can only represent electromagnetic processes somewhat roughly, greater precision being precluded by the discontinuous structure referred to above. Our inability to make any further advances in this connexion at the present time may well be due in the first place to our lack of experimental data (such as may be obtainable from investigations of the processes underlying light emission), and in the second place to the inadequacy of our concepts (probably to that of our concept of energy in particular).

This limitation of our ability to describe microcosmic processes has found expression in the so-called **indeterminacy principle** or **uncertainty principle** of HEISENBERG (1927), which may be enunciated as follows: *The maximum possible accuracy of description of a process is such that the product of the uncertainties in the observed values of the two conjugate quantities measured in order to describe the action* (erg-sec. = gm. cm.^{2} sec.$^{-1}$) *is of the order of magnitude of* h ($= 6{\cdot}55 \times 10^{-27}$ erg-sec.).

To illustrate this principle we shall consider a few examples. Suppose we wish to determine the position of a very small particle (say an electron). In the case of particles which are optically visible we should use a microscope. Now the possibility of determining the exact position of the particle is limited by the wave-length of the light. The width of the diffraction figure, which is to be regarded as the " image " of the particle (see Vol. IV, p. 149), is at least of the order of magnitude of the wave-length of the light used. In order to determine the position of a very small particle like an electron or a proton, it is therefore necessary to use " light " of very short wave-length (" γ-ray microscope "). But the shorter the wave-length, i.e. the greater the frequency ν, the greater is the effect of the momentum of the radiation on the particle (see p. 236) and consequently the less the accuracy with which the momentum of the particle (gm. cm. sec.$^{-1}$), i.e. the conjugate quantity to the position (cm.), can be measured. Thus the more exactly we try to determine the position of the particle (by using light of shorter wave-length), the less accurately are we able (on account of the Compton effect) to determine the momentum of the particle (fig. 26).

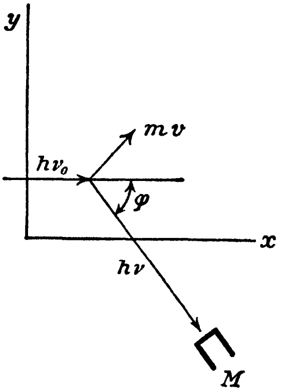

Fig. 26.—Determination of the position and momentum of an electron.

As another example we may consider the passage of cathode rays through a narrow slit (of width *d*). At the moment when the rays pass through the slit, the breadth of the beam is *d*. We may suppose the original beam to have consisted only of particles moving in one direction, i.e. having momentum only in the direction of the beam. At first sight we should expect that the breadth of the beam after passage through the slit would be *d*. Experiments of this kind show, on the contrary, that the electrons are diffracted (see p. 244) and that the beam broadens out after passage through the slit, just as an originally parallel beam of light does. Thus the particles are given a momentum at right angles to the original direction of the beam. Hence if the position of a particle is determined with the uncertainty *d* (i.e. the particle is known to pass through the slit), then an uncertainty arises in regard to its momentum, because of the lateral component which is thereby imparted. This lateral component is indeterminate, being different for different particles. The narrower the slit, the more marked is the diffraction. Hence the greater the accuracy with which the position co-ordinate is determined, the more uncertain does the momentum become.

Let p_1 be the component of momentum at right angles to the original direction of the beam for a particle which is diffracted through the angle θ towards the first diffraction maximum. Then if p_b is the momentum in the original direction of the beam, we have $\tan\theta = p_1/p_b$.

Again, for the first diffraction maximum we have $\sin\theta = \frac{3}{2}\lambda/d$ (see Vol. IV, pp. 199 and 200). Since θ is small, we may take $\tan\theta = \sin\theta$ and also $\lambda = h/p_b$ (p. 246) Hence

$$\frac{p_1}{p_b} = \frac{3}{2}\frac{\lambda}{d} = \frac{3}{2}\frac{h}{p_b d}.$$

The difference between the two values of p_1 corresponding to the two first maxima on either side is therefore $2p_1 = 3h/d$. This may be taken as the uncertainty Δp_1 of the lateral momentum for any particular electron; for an overwhelming majority of the particles lie within this range (cf. fig. 36 on p. 201 of Vol. IV). The uncertainty Δs of the co-ordinate of position in the direction at right angles to the original direction of the beam is the width d of the slit. Hence we obtain

$$\Delta s \Delta p_1 = 3h.$$

Thus the product of the uncertainties of the two conjugate quantities, length and momentum, does actually turn out to be of the order of magnitude of h.

Action may also be considered as the product of the conjugate quantities energy and time. Accordingly a given uncertainty in a determination of time must be associated with an uncertainty in the conjugate determination of energy, and vice versa. Consider, for example, a train of sine waves of unlimited length and of frequency ν, falling on some type of shutter, which is opened and closed in order to determine the time at which the waves pass through. The uncertainty of this determination is thus the interval Δt during which the shutter remains open. Behind the shutter we obtain a section of the wave-train of limited extent. An experimental example of this kind has been discussed on p. 239 in connexion with the periodic interruption of a train of light waves by means of a Kerr cell operated by electrical oscillations. A limited portion cut off from a monochromatic wave-train is no longer monochromatic, but in accordance with its Fourier analysis must be regarded as made up by the superposition of different frequencies. The uncertainty $\Delta\nu$ thus introduced into the frequency becomes greater as the length of the portion of the train cut off is made smaller (i.e. as the frequency of modulation is increased). Now the energy E is related to the frequency ν by the equation $E = h\nu$. Hence an uncertainty in the frequency implies an uncertainty in the energy.

To a first approximation the uncertainty of frequency introduced is twice the frequency of modulation; i.e. $\Delta\nu \approx 2/\Delta t$, where the symbol $\approx$ means " is of the order of magnitude of ". Hence we have $\Delta\nu\Delta t \approx 2$, or

$$h\Delta\nu\Delta t = \Delta E \Delta t \approx 2h.$$

The product of the uncertainties of the conjugate quantities energy and time is thus once more of the order of magnitude of h. The length Δx of the wave-train cut off is $c\Delta t$ and the uncertainty in the wave-number is $\Delta\bar{\nu} = \Delta\nu/c$. Hence we may write $\Delta\bar{\nu}\Delta x \approx 2$.

The same considerations also apply to the passage of a material particle through a shutter device. Here again an uncertainty in the wave-mechanical frequency or wave-length means an uncertainty in the velocity and hence in the kinetic energy of the particle.

The uncertainty attaching to a light quantum may be calculated as follows. The duration of the process of emission is of the order of magnitude of 10^{-8} sec. Hence $\Delta\nu$ is of the order of magnitude of 10^8 sec.$^{-1}$. Now $\nu = c/\lambda$ and therefore $\Delta\nu = -c\Delta\lambda/\lambda^2$. Let us take e.g. the green Hg line ($\lambda = 5461$ Å.). Then we have

$$\Delta\nu \approx 10^8 \approx \frac{3 \times 10^{10}}{(5{\cdot}5 \times 10^{-5})^2}\Delta\lambda,$$

whence

$$\Delta\lambda \approx 10^{-11} \text{ cm.} = 10^{-3} \text{ Å.}$$

This is the "natural" line breadth (see p. 221). From the relation $\Delta\bar{\nu}\Delta x \approx 2$ given above we have, since $\Delta\bar{\nu} = \Delta\nu/c$,

$$10^8 \Delta x = 2 \times 3 \times 10^{10},$$

whence $\Delta x = 600$ cm. Hence if the wave-number (and therefore the energy) of a light quantum is determined with a degree of certainty corresponding to the natural line breadth, the quantum can only be localized within a distance of a few metres measured in the direction of propagation.

Range of Validity of the Indeterminacy Relation.—The relation obviously holds for all processes of an electromagnetic nature, in which h plays a part. On account of the smallness of h, the relation is of no practical significance in macroscopic processes. For very small-scale processes, however, the above examples show that it is of very great importance. In the light of the discovery of the diffraction of electrons and protons (p. 256) it is now probable that the behaviour of all matter is in accordance with wave-mechanical theory (p. 246), i.e. that the quantity h plays a part in all material processes. We must accordingly conclude that *all* processes are subject to the principle of indeterminacy.

This "granular" character of physical phenomena,* as characterized by the constant h, affects all observable processes. In this connexion, however, we must (at least provisionally) make one exception—gravitation. Though gravitation also appears to be a property of electromagnetic energy and its mass (perhaps only another manifestation of the latter), we still know far too little about it to be able to draw any definite conclusions.

The indeterminacy principle is really only another way of expressing the indeterminacy (in space or time) of the wave-processes, emphasizing the special relation to the quantity h. According to this principle, all statements concerning systems of atomic size are necessarily affected by a certain degree of indeterminacy, in so far as they concern single processes. Statistical conclusions concerning a large number of processes can, however, be deduced from wave-mechanics with any desired degree of certainty. Thus, for example, we can never know whether *one particular selected* molecule rebounds in accordance with classical mechanics when it collides with another molecule; but we can and do know that the *average behaviour* for a very large number of molecules is very nearly in accordance with classical mechanics, and the extent of the discrepancy (due to particle diffraction) can be calculated with any desired degree of accuracy.

16. The Wave-mechanical Interpretation of Radioactive Processes

Distribution of Potential near the Nucleus.—The fundamental experimental data are provided by the investigations of RUTHERFORD.

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* This is not to be taken in any material sense, but simply as a convenient way of expressing the fact that all observable elementary processes are discontinuous in character.

In order to understand their interpretation, imagine a positively-charged particle to be gradually brought up towards an atomic nucleus, all the distances involved being small relative to the dimensions of the whole atom. At first the particle will be repelled. According to the experiments referred to on p. 87, these repulsive forces obey the inverse square law down to distances of about 10^{-11} cm. and often even less. On the other hand, at very small distances from the centre of the nucleus forces of attraction must occur; otherwise the nucleus would fly to pieces. Thus the distribution of potential must be of the form shown in fig. 27: the nucleus must be surrounded by a so-called potential barrier. In order to penetrate into the nucleus, a positive particle has to get past this barrier. According to the ordinary laws of classical electrodynamics, it must therefore possess an initial energy which is at least as great as the height of the barrier. Now experiment shows that this is in fact not the case. For example, the investigations of Rausch von Traubenberg (p. 111) prove that protons of very low energy (about 10^4 volts) are able to penetrate into nuclei for which the height of the barrier (as determined by the scattering of α-particles) is of the order of 10^6 volts. At these low energies, however, the probability of penetration is very small. Moreover, the reverse behaviour had been previously observed by Rutherford. In the bombardment of uranium atoms with α-particles from ThC′ (energy $W_\alpha = 14 \times 10^{-6}$ erg) there is no appreciable deviation from the inverse square law. Here the nearest approach to the uranium nucleus is 3×10^{-12} cm. (see p. 84). It is certain, therefore, that the distance of the maximum of the potential barrier (fig. 27) from the centre of the nucleus is less than 3×10^{-12} cm. for uranium, and that its height is greater than 14×10^{-6} erg. A similar distribution of potential also holds for the neighbouring heavy atoms in the periodic table. Yet when uranium disintegrates it emits α-particles with an energy of only $6{\cdot}6 \times 10^{-6}$ erg. Thus although their energy is less than the height of the barrier, α-particles are clearly able to get out of the nucleus, i.e. to get past the barrier. This behaviour corresponds exactly to the penetration of protons of low energy into nuclei. On the basis of classical electrodynamics the phenomenon is unintelligible. Wave-mechanics, however, provides an interpretation of it.

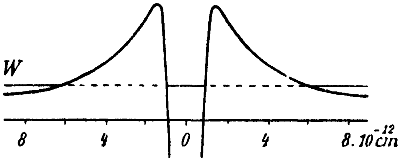

Fig. 27.—Probable form of the potential curve in the neighbourhood of a nucleus

Wave-mechanical Theory of Nuclei.—To take an optical simile (cf. p. 262), the nucleus is like a region of variable refractive index, in which the material waves of bombarding elementary particles are totally reflected. In optical total reflection a part of the wave-motion passes into the reflecting medium, where its presence may be demonstrated by the experiment referred to on p. 58 of Vol. IV. The amplitude of the waves shows a very rapid exponential decrease as the distance from the reflecting interface increases. In the same sort of way, a portion of the material waves passes through the potential barrier. Hence the probability that particles may be encountered on the far side is a finite one. This probability becomes smaller as the energy of the particles is decreased relative to the height of the barrier. Hence radioactive nuclei are clearly those that contain α-particles with an energy which is comparable with the barrier height. From considerations of this sort GAMOW has calculated the probability of the escape of α-particles through the potential barrier of a disintegrating nucleus. The following formula is found for the disintegration constant λ (see p. 23):

$$\log_e \lambda = \frac{16\pi e}{h}\sqrt{m(Z-2)r_0} - \frac{8\pi e^2}{h}\frac{(Z-2)}{v} + \log_e \frac{h}{4mr_0^2},$$

in which e is the mass of an electron, m the mass of an α-particle, r_0 the distance of the maximum of the potential barrier from the centre of the nucleus (i.e. the effective nuclear radius), Z the atomic number of the element under consideration, and v the velocity with which the α-particle leaves the nucleus. Substituting the numerical values and using a mean value for r_0 (namely $r_0 = 10^{-12}$ cm. for the heavy radioactive elements) in the last term, which is insensitive to changes of r_0, we obtain for λ (in sec.$^{-1}$) the expression

$$\log_{10} \lambda = 4{\cdot}1 \times 10^6 \sqrt{(Z-2)r_0} - 1{\cdot}19 \times 10^9 \frac{(Z-2)}{v} + 20{\cdot}47.$$

From this we see that the GEIGER-NUTTALL relationship (p. 23) is only a first approximation. Its comparative accuracy is due to the fact that Z, v, and r_0 are nearly constant for all the radioactive elements. Deviations from the GEIGER-NUTTALL relationship can be understood in the light of the above equation, which is also applicable (after suitable transformation) to artificial transmutation processes. Thus e.g. in fig. 11, p. 24, the point for AcX lies off the GEIGER-NUTTALL line because here the velocity of the α-particles is less than for the preceding element RdAc.

Theory of γ-ray Emission.—The emission of γ-rays which is observed in a large number of radioactive transformations was at first thought to be due to the motion (or rearrangement) of the β-particles (electrons) within the nucleus. Accumulated evidence of various kinds leads, however, to the view that the γ-rays are probably produced in the main by the rearrangement of α-particles or protons. There are two principal lines of inquiry which point in this direction: the investigation of (1) the long-range α-rays emitted with small intensity by

RaC and ThC, and (2) the " fine structure " in the ranges of normal α-rays. The investigation of the γ-rays produced in artificial atomic transmutations also provides evidence in the same direction.

Rutherford and his co-workers were able to show in 1931 that the long-range α-rays from RaC fall into distinct groups with characteristic ranges. By means of the Geiger relationship (p. 17), amplified by a correction term, it is possible to calculate from these ranges the velocities (and hence the energies) of the α-particles in question (see Table XXXII). The energy differences in column five of the table are calculated with due allowance for the recoil (see below).

Table XXXII

Group	Range in Cm.	Energy in Millions of Volts	Relative Number	Energy Difference in Millions of Volts relative to Main Group	$h\nu$ of Observed γ-rays, in Millions of Volts
0	6·88	7·68	10,000,000		
1	7·79	8·30	0·49	0·63	0·61
2	9·04	9·12	16·7	1·46	(1·43)
3	9·50	9·41	0·53	1·76	1·78
4	9·78	9·59	0·93	1·94	
5	10·21	9·84	0·60	2·20	2·22
6	10·46	9·99	0·56	2·35	
7	10·83	10·22	1·26	2·58	
8	11·25	10·47	0·67	2·84	
9	11·52	10·62	0·21	3·00	(3·03)

The remarkable fact emerges that certain of the observed γ-ray frequencies correspond exactly to energy quanta which are equal to the energy difference between long-range α-ray groups and the main α-ray group. (See last column of Table XXXII.*) This may be expressed in the following significant equation:

$$h\nu = E_k - E_n,$$

where $h\nu$ is the γ-ray quantum, E_k the energy of the kth group of long-range α-rays, and E_n the energy of the normal α-rays. The analogy to the Bohr quantum condition for the emission of optical spectra is complete. We are therefore led to conclude that the emission of an α- or β-particle causes a disturbance of the nucleus of such a kind that nuclear α-particles are raised to " excited " energy levels. As the experiments show, these excited levels must be fairly sharply defined. Soon after, the excitation energy is emitted as a γ-ray quantum of corresponding definite energy, the nucleus thereby reverting to its

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* The empty spaces in the last column of the table presumably correspond to γ-rays of such low intensity that they have escaped observation. Observed γ-rays not included in the table may be interpreted as corresponding to energy differences between higher α-ray groups (not between an α-ray group and the main α-ray group).

" normal " state in much the same way as an atom reverts to its normal state by electronic transitions with optical emission.

The subsequent radioactive disintegration for the most part involves nuclei whose α-particles are all in their lowest levels; but a small number of α-particles (if the decay constant is large enough, an observable number) are expelled from higher energy levels, and so constitute the long-range α-particles. Their excess of energy (relative to the normal α-particles and with due allowance for recoil) is thus a measure of the excitation energy of the level in question. The relation to the γ-ray energy quantum follows at once.

The second line of inquiry which leads to the same conclusion is the investigation of the ranges of the normal α-particles. It is found that these fall into groups with very slightly differing velocities. Five such groups are found, for example, for ThC.

This " fine structure " was discovered by measurement of the radii of curvature of the paths of the particles in the very powerful and extensive magnetic fields made available by the large Paris magnet (Rosenblum, 1931). It found that the energy differences between the different groups agree remarkably well with the values of the quanta of the observed γ-rays (e.g. for ThC). For reasons which cannot be discussed here, the long life-period of ThC precludes the theory given above as an explanation of the appearance of different α-ray velocities. Hence we must conclude that after the expulsion of an α-particle the nucleus is left in an " excited " state, and that it subsequently reverts to its " normal " state with emission of a γ-ray quantum. The energy (or range) of the expelled α-particle thus determines the magnitude of the γ-ray quantum (i.e. its frequency); if the former is smaller, the latter is correspondingly greater.

The allocation of γ-rays to differences between energy levels of α-particles within the nucleus appears to be further supported by the observations of Rutherford and his co-workers on actinium emanation. This is found to emit two groups of α-rays with an energy difference of about 340,000 volts, as well as an intense γ-radiation of exactly corresponding frequency. The β-radiation is only feeble.

Experiment shows that (with the exception of RaE and RaF) β-ray changes are also accompanied by intense γ-radiation. So far, however, it has not been possible to extend the theory to cover this phenomenon.

In certain cases of artificial nuclear transmutation (p. 109), notably for Be, γ-rays are found to be emitted (Bothe and Becker, 1930). According to what has been said above, this may be interpreted by supposing that the bombarding proton, on being captured, raises the nucleus into an excited state from which it passes over to the normal state of the new nucleus with emission of a γ-ray quantum.

CHAPTER VI

Molecular Structure

A. MOLECULAR SPECTRA (BAND SPECTRA)

1. General Discussion of Band Spectra

Structure of Band Spectra.—Spectra are often observed which contain so many lines crowded close together that in spectroscopes of small resolution they give the impression of being continuous. Figs. 12 and 13 of Plate XIV, facing p. 160 of Vol. IV, give an idea of the appearance of spectra of this kind, which are referred to as **band spectra.** Closer investigation has shown (see further below) that these bands are emitted by *molecules*, whereas ordinary line spectra are emitted by *atoms*. We are now able, not only to state in many cases the exact chemical molecule to which a given band spectrum belongs, but also to deduce from the band spectrum certain important physical and chemical properties of that molecule. Molecular spectra usually show a characteristic distribution of intensity, there being several more or less narrowly bounded spectral regions in which the intensity falls off (either towards longer or towards shorter wave-lengths) from a certain definite point called the *head of the band*. The band is said to be degraded towards the red or towards the blue, as the case may be. The general appearance is often that of a channelled or fluted band, though in spectrographs of very high dispersion the " bands " prove to be built up of lines arranged with great regularity. These lines form an array which often stretches in both directions from a gap in the band (see fig. 1).

A *band*, then, is an assemblage of a large number of *lines*. A large number of bands together form a *band system*, and, finally, several such band systems may be comprised in the complete spectrum of a given molecule under given conditions of excitation.

It has been found possible to recognize this threefold structure in almost all cases of molecular spectra. The band systems, which may consist of only a few bands or of well over a hundred, may lie in different regions, e.g. one system in the visible and one in the ultra-violet. Each of these systems is found to be built up of a regular array of bands, and each of the bands in turn to be built up of regular arrays of lines. In certain circumstances neighbouring bands may overlap, thus obscuring the regularity of arrangement of the lines and making the analysis very difficult.

A number of items of evidence may be adduced to prove that the bands of a system all belong to the same molecule. Thus they are all similarly influenced by an alteration of the conditions of excitation, and in particular disappear simultaneously when the conditions are such that the chemical individual to which they are due must be supposed to have ceased to exist in the system. Again, they all have the same general appearance, being all degraded towards the same side. Most important, however, there are relatively simple relationships between them (see below). The occurrence of band systems in different spectral regions, on the other hand, is somewhat less regular and depends very much on the conditions of excitation. Hence the relation between band systems situated in widely separated spectral regions can usually be established only by a close analysis of their structures.

Now it is remarkable that a threefold character is also found in connexion with the spectral regions in which molecular emission or absorption of radiation occurs. Thus many molecules are known to give spectra in the far infra-red (about 150μ to 30μ) and in the near infra-red (about 5μ to 1μ), in addition to the abovementioned band spectra in the visible and ultraviolet. The spectra in all three regions belong to the same molecular species. Moreover, it is found that the absolute frequencies of the infra-red groups are of the order of magnitude of the frequency *differences* occurring in the corresponding visible and ultra-violet band spectra. Thus the average frequency of the group in the far infra-red is approximately equal to the frequency differences between the *lines within a band*; while the frequency of the group in the near infra-red is approximately equal to the frequency differences between the *bands within a band system.*

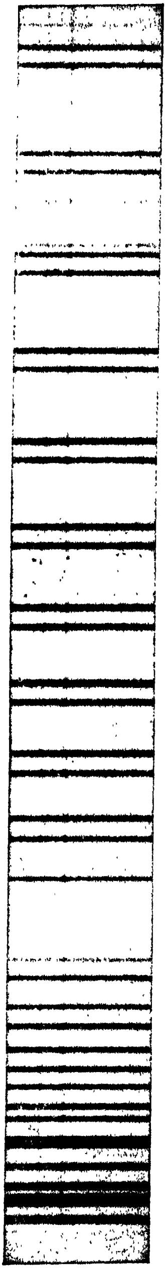

Fig. 1.—Band spectrum of O_2 under great dispersion

[From *Handbuch der Physik*, Vol. XXI (Springer, Berlin).]

The facts enumerated below show that the longest-wave spectra (far infra-red) are connected with the rotations of the molecules—so-called **pure rotation spectra**—while the shorter-wave infra-red spectra are connected with the internal vibrations of the molecules, upon which are superimposed the rotational motions just referred to — so-called **rotation-vibration spectra.** Finally, the complete band spectra (visible and ultra-violet regions) are connected with electronic transitions which determine their spectral region, the band systems being connected with the superimposed molecular vibrations and the individual bands being connected with the superimposed rotations of the molecules.

Model of a Diatomic Molecule.—In order to illustrate the above interpretation, we shall consider the possible states of internal energy of a diatomic molecule. As far as mechanical properties are concerned, we may provisionally regard such a model as consisting of two spheres connected rigidly together, the distance between them being large compared with their diameters (dumb-bell model, cf. Vol. II, p. 45). The internal energy of a model of this kind consists entirely of its energy of rotation E_r. According to p. 138 of Vol I, this is $\frac{1}{2}I\omega^2$, where I is the moment of inertia involved and ω is the angular velocity. Introducing the angular momentum $J = I\omega$ (see Vol. I, p. 136), we have $E_r = \frac{1}{2}J^2/I$. Here $I = \frac{m_1 m_2}{m_1 + m_2} r^2$, where m_1 and m_2 are the masses of the two atoms of the molecule and r is the distance between them.

Of the possible rotations, there occur at ordinary temperatures only those for which the moment of inertia has a sufficiently high value. For example, rotation about the axis of the molecule (i.e. the line joining the two atoms) obviously does not occur, as is proved by the absence of the corresponding degree of freedom in connexion with the specific heats of diatomic gases (see Vol. II, p. 45; also this volume, Chap. VII, p. 412).

The assumption that the two atoms are rigidly connected together is certainly too specialized. A study of specific heats shows that new degrees of freedom appear at sufficiently high temperatures. The atoms must be supposed to be connected together as by a spring, so that any deformation (i.e. alteration of the distance between them due to collisions, absorption of energy, &c.) causes the nuclei to vibrate relative to one another. The observed variations of specific heat indicate that these vibrations are associated with rather large energies in comparison with the ordinary thermal energy. The vibrations may be either harmonic or markedly anharmonic; in the former case the frequency will be independent of the amplitude, in the latter it will vary markedly with the amplitude.

The third possible way in which the internal energy of a molecule may change is by a change of the electronic configuration similar to those discussed for atoms. The corresponding energies are of the same order of magnitude as those for atoms, and as a rule, therefore, the corresponding spectral emission lies in the visible or ultra-violet region.

2. Pure Rotation Spectra

Experimental.—In the long-wave infra-red it is possible to observe absorption spectra consisting of lines at approximately equal distances apart on a frequency scale. Spectra of this kind are given by the molecules HF, HCl, HBr, and HI. (The molecules H_2O and NH_3 also show complicated absorption spectra in this region.) As was shown by Czerny (1925 and 1927), the observed arrays of lines can be represented by the following equations, the unit of wave-number being $cm.^{-1}$.

$$\text{HF:}\ \tilde{\nu} = 41{\cdot}086\ \mathrm{M} - 0{\cdot}011879\ \mathrm{M}^3;\ \mathrm{M} = 2, 4, 5.$$
$$\text{HCl:}\ \tilde{\nu} = 20{\cdot}8411\ \mathrm{M} - 0{\cdot}001814\ \mathrm{M}^3;\ \mathrm{M} = 4, 6, 7, 8, 9, 10, 11.$$
$$\text{HBr:}\ \tilde{\nu} = 16{\cdot}7092\ \mathrm{M} - 0{\cdot}001457\ \mathrm{M}^3;\ \mathrm{M} = 5, 6, 7, 10, 11, 12, 13, 14.$$
$$\text{HI:}\ \tilde{\nu} = 12{\cdot}840\ \mathrm{M} - 0{\cdot}000820\ \mathrm{M}^3;\ \mathrm{M} = 6, 7, 8, 9.$$

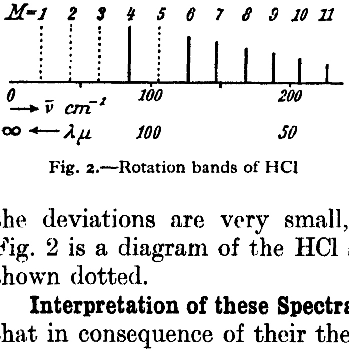

Fig. 2.—Rotation bands of HCl

Thus M assumes successive integral values. No absorption investigations have been carried out at longer wave-lengths, but the occurrence of lines with M-values still smaller than those given may be anticipated. As may be seen from the formula, the line for HI with M = 1 must lie at a wave-length of nearly 1 mm., i.e. in the region of ultra-short electric waves. The distances between neighbouring lines are not quite constant, owing to the second term in the formulæ; but the deviations are very small, especially for the heavier halogens. Fig. 2 is a diagram of the HCl spectrum. Lines not yet observed are shown dotted.

Interpretation of these Spectra.—Specific heat investigations indicate that in consequence of their thermal agitation molecules must possess internal energy in addition to kinetic energy of translation. The measurements lead to the rigid dumb-bell model as a first approximation for diatomic molecules, the dumb-bell being able to execute rotations (see Vol. II, p. 45) about an axis normal to the line joining the two atoms. If such a diatomic molecule possesses an electric dipole moment (i.e. if its constituent charges are distributed unsymmetrically relative to the axis), it may be expected to send out electromagnetic waves when it rotates, i.e. to have a rotation spectrum. The sharpness of the lines actually observed indicates that only certain quite definite energy states of the molecule are permitted. Since we are dealing with a rotator, we may expect the angular momentum $\boldsymbol{j}_r$ to be determined by an integral quantum number j_r according to the formula $|\boldsymbol{j}_r| = \sqrt{j_r(j_r+1)}\,\frac{h}{2\pi}$ (see p. 312). Hence, according to the formula of p. 363, the energy of rotation will be given by

$$E_r = j_r(j_r+1)\frac{h^2}{8\pi^2 I} + \text{constant},$$

where $j_r = 0, 1, 2 \ldots$. The wave-number $\bar{\nu} = \nu/c$ of a line of the pure rotation emission spectrum corresponding to the quantum transition $(j_r + 1)$ to j_r is given by

$$\frac{E_{j_r+1} - E_{j_r}}{hc} = [(j_r+1)(j_r+2) - j_r(j_r+1)]\frac{h}{8\pi^2 Ic} = \frac{(j_r+1)h}{4\pi^2 Ic}.$$

Since j_r may have any integral value, transitions in which j_r changes by unity (see selection rule below) will therefore give rise to an array of lines at equal distances apart on the wave-number scale. Inserting the observed value for HCl, for example, and remembering that $h/(4\pi^2 c) = 55{\cdot}4 \times 10^{-40}$ c.g.s. units, we obtain $I = 2{\cdot}64 \times 10^{-40}$ gm. cm.^{2}. Now we know that $I = \frac{m_1 m_2}{(m_1 + m_2)} r^2$, where m_1 and m_2 are the masses of the H atom and Cl atom respectively and r the distance between them in the HCl molecule. The mass of a single atom is its atomic weight divided by Avogadro's number. Hence we may calculate r from the above value of I. The value obtained is $r = 1{\cdot}28 \times 10^{-8}$ cm. The very good agreement of this with the figures obtained by other methods furnishes confirmation of the interpretation of the far infra-red spectra as due to the rotation of the molecules. It also proves the validity of the application of the general quantum condition to the rotational transitions of a diatomic molecule.

We have still to give a quantitative theory of the small correction terms which account for the departures from equal spacing in the lines of the pure rotation spectra. The cause of these departures is to be found in the fact that, as the velocity of rotation increases, the centrifugal force must increase the distance r between the atomic nuclei and hence increase the moment of inertia I. As a result the energy levels corresponding to higher j_r-values must lie somewhat lower than in the simple theory above. The lines corresponding to transitions involving higher j_r-values must therefore have somewhat lower wave-numbers than they would have if I were constant. The more detailed calculation shows that the diminution of wave-number is proportional to $(j_r + 1)^3$. Thus this theory is able to account very satisfactorily for the observed facts, the quantity M of the empirical formulæ being seen to stand for $(j_r + 1)$. From the value of the coefficients of M^3 it is possible to draw conclusions as to the "elasticity" of the linkage between the atoms in the molecule.

Selection Rule.—Since the rotation of the molecules is uniform, the Fourier analysis involves only terms of the first order, and consequently according to p. 196 only those lines for which $\Delta j_r = \pm 1$ are to be expected. This is in agreement with the observation that the lines of the pure rotation spectra are single; for on account of the change in the moment of inertia with j_r, the lines corresponding to transitions for which $\Delta j_r > 1$ would lie very close to those corresponding to transitions for which $\Delta j_r = 1$ with other values of j_r. This may best be seen by drawing a system of energy levels. Actually the fine structure to which transitions with $\Delta j_r > 1$ would thus give rise is not observed.

3. Rotation-vibration Spectra

Empirical.—In addition to the above absorption spectra in the far infra-red, the hydrogen halides also possess absorption bands in the shorter-wave infra-red between 5μ and 1μ. The general structure of a typical band of this sort is shown in fig. 3. The form is seen to be double (so-called *double band*) in the sense that a curve drawn through the intensity maxima of the individual lines shows two maxima. The wave-numbers of the individual line maxima are very well represented by the formula

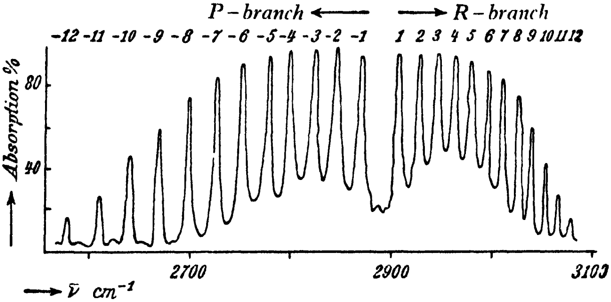

Fig. 3.—Coarse structure of the rotation-vibration band of HCl at about $3{\cdot}46\mu$

$$\tilde{\nu} = 2886{\cdot}20 + 20{\cdot}5379\,\mathrm{M} - 0{\cdot}30318\,\mathrm{M}^2 - 0{\cdot}001814\,\mathrm{M}^3.$$

When apparatus of greater resolving power is used, the lines are found to possess a fine structure. The whole bands then present a very regular appearance like that shown in fig. 4, which gives the results of recent measurements. The distance between the lines is approximately equal to that between the lines of the pure rotation spectra (20·5 cm.$^{-1}$ as compared with 20·8 cm.$^{-1}$). This indicates the physical cause to which the bands are due, namely the vibrations of a molecule with a dipole moment, and (superimposed upon these) the rotations. For this reason these bands in the near infra-red are known as *rotation-vibration bands.*

Theory of the Bands.—In order to understand the observed regularities of structure, we shall consider in detail the mechanism underlying bands of the kind under consideration. The individual lines are due to transitions of the molecule from one energy state to another in accordance with the fundamental relation $h\nu = E_1 - E_2$. Thus we have first to consider the possible energy states of a diatomic molecule, which we may think of as a dumb-bell consisting of two heavy spheres joined together by a spiral spring. Such a model can possess both vibrational and rotational energy at the same time. The sharpness of the observed spectral lines indicates that we have to deal with quantized states. The vibrational energy E_v of the molecule is that of an oscillator, i.e. according to p. 264 is given by $E_v = (n_v + \frac{1}{2})h\nu_0$, where ν_0 is the vibrational frequency (the vibrations being assumed harmonic) and n_v is a quantum number which can assume integral values only. Neglecting rotation for the time being, we shall expect to find spectral lines corresponding to transitions from one vibrational state (characterized by the quantum number n_v') to another (characterized by n_v''). The frequencies of these lines will be given by the relations:

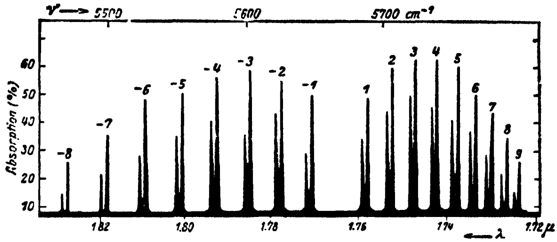

Fig. 4.—Rotation-vibration band of HCl at about 1·77μ, showing the fine structure under high resolution

[From Eucken, *Lehrbuch der chemischen Physik* (Akademische Verlagsgesellschaft, Leipzig).]

$$\nu_v = \frac{E_v' - E_v''}{h} = (n_v' - n_v'')\nu_0.$$

According to this the frequencies (or wave-numbers) of the vibrational lines (each of which, as we saw above, is really a double band) must be integral multiples of a fundamental value. Actually this is found to be only approximately true. The reason for the discrepancy lies in the departure of the vibrations from pure harmonicity. As we need not prove in detail here, the energy of an anharmonic oscillator to a first approximation is $E_v = (n_v + \frac{1}{2})h\nu_0[1 - x(n_v + \frac{1}{2})]$, where x is a measure of the anharmonicity. The observed facts can be well accounted for by expressions of this kind.

Upon this vibrational motion is superimposed the rotation of the molecule. We have seen on p. 366 that the rotational transitions are limited by the selection rule $\Delta j_r = \pm 1$. In the case of the anharmonic oscillator, on the other hand, the Fourier analysis contains terms of all orders, and hence transitions can occur in which the vibrational quantum number n_v changes by any integral amount. The individual lines of a rotation-vibration band corresponding to the vibrational transition $n_v' \rightarrow n_v''$ will therefore be given by

$$\nu = \frac{E_v' + E_r'}{h} - \frac{E_v'' + E_r''}{h} = \nu_v + \frac{E_r' - E_r''}{h},$$

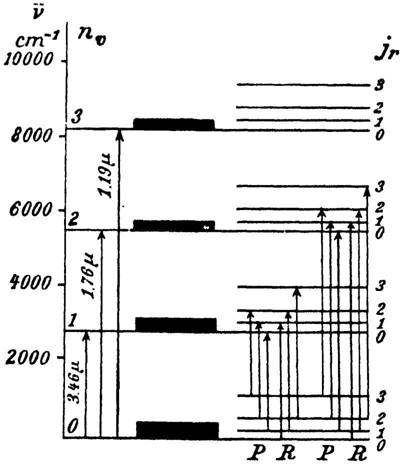

Fig. 5.—Energy levels involved in the rotation-vibration spectrum of HCl

On the right: rotational levels, much magnified. On the left: vibrational levels: the black regions comprise about 15 rotational levels.

where E_r' and E_r'' are the rotational energies of the initial and final states respectively, and ν_v is the frequency of the line to be expected from the pure vibrational transition without alteration of rotational energy. In fig. 5 this is represented in the form of a system of energy levels. Only four vibrational levels are shown ($n_v = 0, 1, 2, 3$) and only three rotational levels ($j_r = 1, 2, 3$) above each of them. Thus each vibrational level acquires a fine structure by the superposition of the rotational levels. The distance between successive vibrational levels is of the order of 1000 cm.$^{-1}$, while that between successive rotational levels is only of the order of 10 cm.$^{-1}$. Consideration of the diagram leads us to expect, for each vibrational transition, a central line corresponding to the pure vibrational change without alteration of the rotational energy, and on either side of this a symmetrical array of lines at approximately equal intervals, corresponding to different rotational transitions. The array extending towards greater frequencies must (as may be seen from the formula) correspond to changes in the rotational energy for which (in absorption) the quantum number j_r *increases* by unity—the so-called *R-branch*. Similarly the array extending towards smaller frequencies must correspond to changes in rotational energy for which (in absorption) j_r *decreases* by unity—the so-called *P-branch*. The corresponding transitions are indicated by arrows in fig. 5. A glance at figs. 3 and 4 (p. 366) shows that the observed spectra differ in some respects from those anticipated. In the first place, the central line corresponding to the pure vibrational transition is absent (so-called *missing line*). This indicates that the molecule cannot alter its vibrational energy without a *simultaneous* alteration of its rotational energy. This can be understood in the light of the correspondence principle if rotation and vibration occur in a plane. ($\Delta j_r = 0$ is forbidden—a selection rule somewhat analogous to the rule $\Delta l \neq 0$ in atomic spectra.) The central line may, however, appear for more complicated molecules, and its permissibility is then again intelligible on the correspondence principle.

Another feature of the observed rotation-vibration spectra is that the distance between successive lines is not constant, but decreases as we pass to higher wave-numbers.

This systematic alteration of the distance between the lines of a rotation-vibration band must be due to the alteration of the moment of inertia of the molecule (see p. 365). The mean moment of inertia of a vibrating molecule must be expected to differ from that of the molecule when not vibrating. Moreover, the centrifugal force which comes into play during rotation must alter the strength of the linkage between the atoms and so must affect the vibrations. There must therefore be an interaction between vibration and rotation. This can in fact be calculated, and the observed variations of the spacing of the lines can be well accounted for.

Effect of Isotopy.—The above considerations provide a satisfactory explanation of all the observed features except one—the doubling of the lines for HCl (clearly visible in fig. 4, p. 367). It can be easily proved that this doubling is due to the isotopy of chlorine, i.e to the existence of two sorts of chlorine atoms with atomic weights of 35 and 37 respectively.

If the mass of an oscillating body is increased, the elastic forces being kept constant, the frequency is lowered (cf. the effect of loading of a tuning fork with a pellet of adhesive wax). Thus we must expect the vibrational frequency of HCl^{37} to be lower than that of HCl^{35}. Now the isotopes are present in ordinary chlorine in the approximate ratio $Cl^{37} : Cl^{35} = 1 : 3$. Hence the intensities of their respective effects may be expected to be in this ratio. The data represented in fig. 4, p. 367, prove that this is indeed the case for the two components of each line. The frequency difference between the components can also be calculated. The frequency of vibration of a diatomic molecule is given by the formula

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}},$$

in which f is the restoring force per unit displacement and μ is the reduced mass calculated according to the equation

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2},$$

where m_1 and m_2 are the masses of the two atoms. Since the electronic configuration is the same for both isotopes, the value of f is the same for both. It follows that the ratio of the two frequencies is equal to the inverse ratio of the square roots of the reduced masses. The relative difference between the frequencies for HCl^{35} and HCl^{37} (i.e. the ratio of the actual difference to the frequency of either) is therefore given by

$$\frac{\delta\nu}{\nu} = \frac{\nu_{35} - \nu_{37}}{\nu_{35}} = 1 - \sqrt{\frac{\mu_{35}}{\mu_{37}}} \sim \frac{1}{1300}.$$

In the band shown in fig. 4, p. 367, the average value of ν is about 5600 cm.$^{-1}$, while the observed value of $\delta\nu$ is about 4 cm.$^{-1}$. The agreement with theory is seen to be very good. The moment of inertia of the molecule also depends on the masses of the atoms, and is therefore different for the two isotopes. A fine structure is therefore to be expected in pure rotation spectra as well as in band structure due to rotation. These fine-structure separations are small, but have been observed in certain cases.

The effect of isotopy upon vibrational frequencies provides an extremely important means, not only of detecting the presence of isotopes, but also of determining their masses. Both as regards sensitiveness and accuracy this method can compete with the direct mass-spectrograph method (p. 99), and in many cases has indeed proved superior to it.

4. Molecular Spectra involving Alterations of Electronic Energy

Band spectra also occur (both in emission and in absorption) in the visible and ultra-violet regions. Probably the best known is the cyanogen band spectrum which is situated in the violet and always occurs in the spectrum of an electric arc between carbon electrodes. It consists of several groups of bands, each of which consists in turn of several partial bands extending towards shorter wave-lengths from sharply defined " heads " (see fig. 6). Under greater resolution these partial bands are found to have a very regular structure of sharp lines (see fig. 7). As a result of the most varied experiments on their excitation and on the properties of the parent molecule, these bands have been shown to belong to the compound CN. The distances between the partial bands is of the order of magnitude of the vibrational frequency of the molecule, while the spacing of the lines in the bands is of the order of magnitude of the rotational frequencies. It is there-

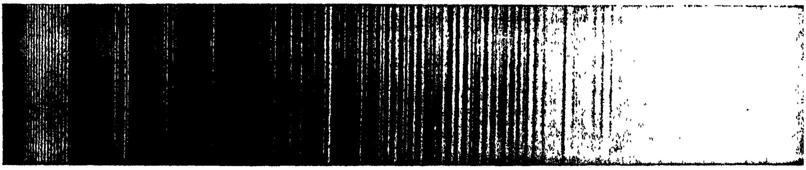

Fig. 6.—Cyanogen bands

[From *Handbuch der Physik*, Vol. XXI (Springer, Berlin).]

fore assumed (this assumption will be fully justified below) that the bands are rotation-vibration bands associated with a simultaneous alteration of the electronic configuration of the molecule. The relatively large energy difference involved in the electronic transition determines the general position of the spectra, namely, in the visible or ultra-violet, which, as we know from atomic spectra, is the spectral region corresponding to transitions of this kind.

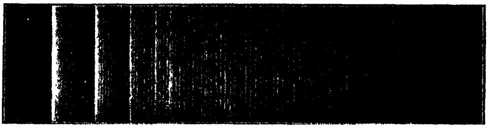

Fig. 7.—Group of bands in the cyanogen spectrum at about $\lambda = 3883$ Å.U. $\Delta n = 0$

[From Graff, *Grundriss der Astrophysik* (Teubner, Leipzig).]

Thus three sorts of molecular energy are involved in the emission of each line: the electronic, the vibrational, and the rotational. Each electronic configuration is associated with a system of vibrational and rotational levels like that shown in fig. 8. The energy of the molecule is determined for the most part by the electronic configuration, but instead of one level we have in the first place a series of levels, according to the magnitude of the quantized vibrational energy. These are shown in the figure to the left, the vibrational quantum number being here denoted by v. Each vibrational state is in turn associated with a series of levels according to the magnitude of the quantized rotational energy. In the figure the vibrational levels shown on the left are drawn again on the right, each with its rotational levels. In the shaded region above the dotted vibrational level on the left the molecule decomposes as a result of its energy of vibration. The figure represents a case in

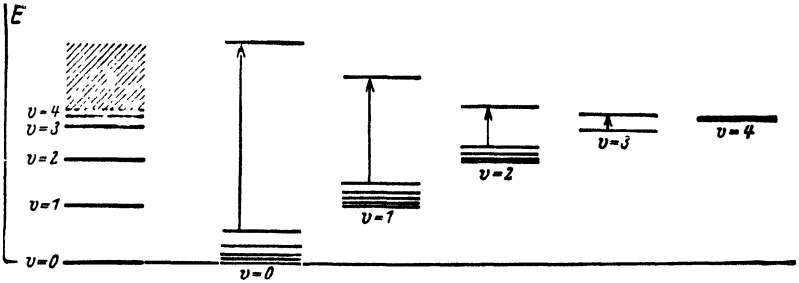

Fig. 8.—General diagram of the energy levels of a molecule (not to scale)

[From *Handbuch der Experimentalphysik*, Supplementary Vol. I (Akademische Verlagsgesellschaft, Leipzig).]

which the energy of the molecule when rotating as well as vibrating may exceed the critical value for vibration alone. The upper levels at the tops of the arrows on the right represent the maximum possible rotational energies for the respective vibrational states. Above these levels the molecule flies to pieces as a result of its energy of rotation.

In the case of rotation-vibration spectra we have seen that the simultaneous occurrence of rotation and vibration affects the rotational and vibrational states to a considerable extent. This was particularly noticeable in the rapid decrease of the spacing of the rotational lines with increase of frequency. The effect of alterations of the electronic configuration is very much greater. Often, indeed, we may speak of completely different molecules, having different strengths of linkage and different moments of inertia, according as we are dealing with an excited or a non-excited state.

A particular band system corresponds to a large number of transitions, all of which have a common initial electronic level and a common final electronic level. This is proved by the experimental conditions under which the system is produced and by the fact that the whole system behaves in the same way if these conditions are altered. The electronic transition, i.e. the magnitude of the change of electronic energy, fixes the general spectral position of the system as a whole. Thus, for example, in addition to the violet system of cyanogen bands mentioned above there is also a red system, which is ascribed to a different electronic transition (p. 379).

The Rotational Structure of the Bands.—In rotation-vibration bands (in the near infra-red, see above) we have two approximately symmetrical branches, the P-branch and the R-branch, extending on either side of the "missing line". As we mentioned above, visible and ultra-violet band-spectra involve transitions between different electronic states in which the distances between the atomic nuclei (and hence the moment of inertia), being dependent on the forces linking the atoms and therefore on the electronic configuration, vary considerably. In addition, the electronic motions in general possess a resultant angular momentum which combines vectorially with that of the rotation of the molecule as a whole. In considering the coarse structure, however, this angular momentum may be neglected. Let the rotational energies of the initial and final states be respectively

$$E_r' = \frac{h^2}{8\pi^2 I'} j_r'(j_r' + 1) = B'chj_r'(j_r' + 1)$$

and

$$E_r'' = \frac{h^2}{8\pi^2 I''} j_r''(j_r'' + 1) = B''chj_r''(j_r'' + 1).$$

Then the wave-number $\bar{\nu}$ of the emitted line is given by

$$\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v + B'j_r'(j_r' + 1) - B''j_r''(j_r'' + 1),$$

where $\bar{\nu}_e$ and $\bar{\nu}_v$ are the contributions due to the changes of electronic and vibrational energy respectively. In this connexion it should be noted that the presence of an angular momentum of the electronic configuration renders permissible transitions *without* alteration of rotational state, so that $\Delta j_r = 0$ is no longer forbidden (compare p. 366). Denoting by j the rotational quantum number of the *final* state (i.e. j_r'' in the above equation for $\bar{\nu}$), we have:

for $\Delta j_r = +1$: $\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v + (B' - B'')j^2 - (B' + B'')j$;

for $\Delta j_r = 0$: $\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v + (B' - B'')j^2 + (B' - B'')j$;

for $\Delta j_r = -1$: $\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v + (B' - B'')(j + 1)^2 + (B' + B'')(j + 1)$.

Thus here there are in general *three* branches. They are known as the P-, Q-, and R-branches respectively. The quantum number j of the final state of the transition may assume any positive integral value, including zero, except in the case of the P-branch ($\Delta j_r = +1$), where the smallest value of j is clearly 1 (transition $0 \rightarrow 1$). Adopting the conventions

$$\bar{\nu}_e + \bar{\nu}_v = A, \quad B' + B'' = 2B, \text{ and } B' - B'' = C,$$

we obtain for the P-, Q-, and R-branches respectively

$$\bar{\nu}_P = A - 2Bj + Cj^2;$$

$$\bar{\nu}_Q = A + Cj + Cj^2;$$

$$\bar{\nu}_R = A + 2B(j + 1) + C(j + 1)^2.$$

If the moments of inertia in the initial and final states are equal, i.e. if $C = B' - B'' = 0$, the Q-branch reduces to a single line with $\bar{\nu}_Q = A$, while the other two branches extend asymmetrically (see formulæ) on either side. In this case the spacing of the lines in the P- and R-branches is uniform, since the terms in j^2 vanish.

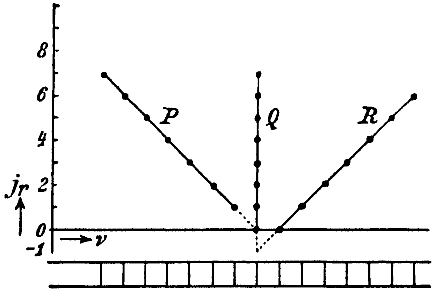

Fig. 9.—Fortrat diagram of a band (C = o)

The structure of a band can best be represented by means of a diagram of the kind first used by FORTRAT. Wave-numbers are plotted as abscissæ and j-values as ordinates (so-called *Fortrat diagram*). Fig. 9 shows the special case ($C = 0$) just mentioned. The corresponding spectral lines are indicated below the diagram on the same wave-number scale.

Actually, as we stated above, the moments of inertia in the initial and final electronic states generally differ markedly, so that C has a value different from zero. Consequently the quadratic terms in the expressions for $\bar{\nu}$ do not vanish. Their effect becomes especially pronounced for the higher values of j. In the normal case the moment of inertia in the initial state of higher excitation is greater than that in the final lower state; for the higher excitation means that the electrons are on the whole farther from the nuclei, which as a rule means that the linkage is weakened and the nuclei move farther apart. Here $I' > I''$, so that $B' < B''$ and C is *negative*. The corresponding FORTRAT diagram is shown in fig. 10. Owing to the negative value of C and the preponderance of the quadratic terms for high values of j, the R-branch bends back as shown in the figure. As we see from the spectral lines below the diagram, there is a crowding together at the right-hand end (the so-called *band head*). The band extends from this head towards the left (i.e. in the direction of decreasing $\bar{\nu}$). Such a band is said to be *degraded to the red*. Degradation in the opposite direction is obtained when C has a *positive* value, i.e. when the moment of inertia of the molecule is greater in the final state than in the initial state of the transition. In this case an increase of the average distance of the electrons from the nuclei *increases* the strength of the linkage between the atoms. The formulæ show that here it is the P-branch that bends back at the higher values of j. The head of the band is thus on the red side and the band is *degraded to the violet*.

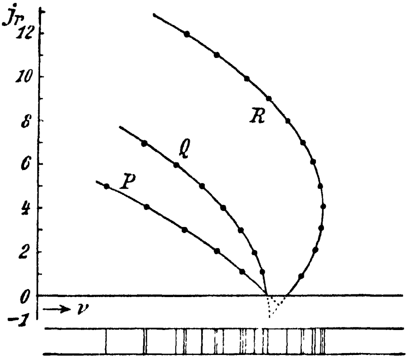

Fig. 10.—Fortrat diagram of a band (C < 0)

Analysis of the partial band with its head at 3883 Å. in the cyanogen system shown in fig. 6, p. 370, gives 2B = 3·843 cm.$^{-1}$ and C = 0·0673 cm.$^{-1}$. The bands of this system have no Q-branch. The smallness of C indicates that B′ and B″ are very nearly equal, i.e. that the moments of inertia of the molecule in the initial and final states are nearly the same. Under these circumstances it is sufficient to calculate an average moment of inertia I_m. According to p. 365 we have

$$I_m = \frac{h}{8\pi^2 cB} = \frac{6\cdot55 \times 10^{-27}}{12\pi^2 \times 3\cdot843 \times 10^{10}} = 1\cdot44 \times 10^{-39} \text{ gm. cm.}^2.$$

Substituting the known masses of the C and N atoms in the equation

$$I_m = \frac{m_1 m_2}{(m_1 + m_2)} r^2,$$

we obtain the value $r = 1{\cdot}16 \times 10^{-8}$ cm. for the distance between the atoms in the CN molecule. This is of the order of magnitude to be expected from other considerations. It is also of interest to work out the magnitude of the linear velocity of the nuclei when they are rotating with the rotational frequency corresponding to the lowest rotational state. The value obtained is about 100 metres per sec.

Distribution of Intensity.—As may be seen from figs. 3 and 4, p. 366, the intensities of the rotational lines in rotation-vibration spectra increase to a maximum as j_r increases and then fall off again. This is due to thermal motions. Just as in the case of translational energy, where at each temperature there is a most probable velocity (see Vol. II, fig. 5, p. 48), so also there is a most probable rotational energy at each temperature. All the other rotational energies, larger and smaller, occur less frequently. The smaller the distance between the energy levels, the higher is the value of j_r corresponding to the most probable energy for a given temperature. In many spectra the intensity maximum lies at a j_r-value near to that at which the P- or R-branch turns back (see fig. 10, p. 374). Hence the intensity is at its greatest by far at the band head. For this reason measurements on bands were formerly referred to the band head; but as we have shown above, the position of the head is not of very fundamental significance. Not until the measurements were referred (originally by HEURLINGER) to the band origin (i.e. the line for which $j_r = 0$ in the Q-branch) could the regularities of the band structure be fully brought to light.

This distribution of rotational energy is also the reason for the non-occurrence of rotation of a diatomic molecule about the line joining the nuclei as axis. The moment of inertia I_x about this axis is extremely small in comparison with the moment I considered above, which refers to a perpendicular axis. Hence the rotational energy

$$E_r = \frac{h^2}{8\pi^2 I_x} j_r(j_r + 1)$$

is so high, even in the lowest rotational state ($j_r = 1$), that an appreciable number of molecules could only be found in this state at extremely high temperatures, i.e. under conditions where the molecules would probably no longer be stable. Thus we see that the allocation of a restricted number of degrees of freedom, as in the treatment of specific heats, depends ultimately on the quantized behaviour of the molecules in question. The very early conclusions of BOLTZMANN therefore held the germ of the quantum theory—a fact which, as is shown by remarks in his papers, BOLTZMANN himself dimly realized (see footnote to p. 150).

In consequence of the statistical energy distribution, the distribution of intensity in the rotational lines depends on the temperature. At low temperatures only the levels with low quantum numbers are present in appreciable proportion; and at a given temperature the preferred levels are lower the greater energy differences between the levels, i.e. lower for molecules with lower moments of inertia. The moment of inertia of H_2, for example, is particularly small, on account of the small mass of the H atom. Here even the first rotational level ($j_r = 1$) is relatively high, several hundred cm.$^{-1}$ as compared with about 20 cm.$^{-1}$ for HCl (cf. p. 364). Hence at very low temperatures only a very small proportion of H_2 molecules possess even *one* rotational quantum. This means that rotation is practically absent, and with it the corresponding degree of freedom. Thus at moderately low temperatures the H_2 molecule behaves, as regards specific heat, as a monatomic gas (see Vol II, p. 45).

The magnitude of the *vibrational* frequency of molecules, which for H_2 is about 2000 cm.$^{-1}$, at once makes it clear why molecules can be regarded as rigid structures (e.g. rigid dumb-bells) for considerations of specific heat. For as a result of the statistical distribution of energy amongst all the degrees of freedom, only a small proportion of the molecules will have an energy corresponding to these large vibrational frequencies. A frequency of 1000 cm.$^{-1}$ corresponds to the mean energy of a gas molecule at 1000° Abs. (see Table XVI, p. 179). Only at very high temperatures, therefore, will the number of vibrating molecules become sufficient to cause an appreciable rise in the specific heat.

Vibrational Structure of the Bands.—The energy level diagram of the CN molecule shows that the vibrational levels are not equally spaced. This is due to the slight anharmonicity of the linkage (p. 369). If we neglect the rotational structure, the regularities of the vibrational structure of a band system can best be studied by considering the position of the band origins. A less accurate but more convenient method is to consider the band heads (fig. 11). As was first shown by Deslandres, the wave-numbers of the band origins (or, less accurately, of the band heads) can be represented by an equation of the form

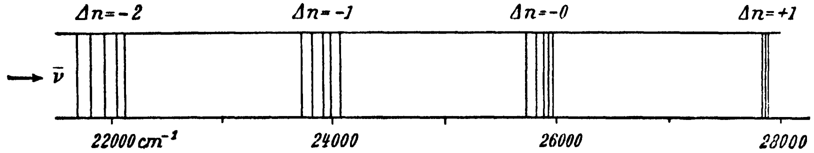

Fig. 11.—Analysis of the band heads of the cyanogen spectrum

Wave-numbers in cm.$^{-1}$

22142	24072	25967	27894
22059	23986	25933	27878
21957	23911	25886	27847
21837	23820	25826	
21705	23713	25739	

$$\bar{\nu} = a + bn + cn^2,$$

in which n has integral values. In order to understand the physical significance of the constants a, b, and c of this equation, we shall consider the mechanism of production of the lines. We have already represented the lines of a band by a general expression involving three constants. The wave-numbers in the Q-branch are given by

$$\bar{\nu}_Q = A + Cj + Cj^2.$$

If we neglect rotation, the wave-number of the band origin ($j = 0$) is given by

$$\bar{\nu} = A = \bar{\nu}_e + \bar{\nu}_v$$

(see p. 372). Now, using the energy formula for an anharmonic oscillator (see p. 367), we may write $\bar{\nu}_v$ in the form

$$\bar{\nu}_v = (n_v' + \tfrac{1}{2})\nu_0'[1 - x'(n_v' + \tfrac{1}{2})] - (n_v'' + \tfrac{1}{2})\nu_0''[1 - x''(n_v'' + \tfrac{1}{2})],$$

in which quantities with a single dash refer to the initial state and quantities with a double dash refer to the final state. If n_v'' is kept constant, we get a so-called n_v'-progression, the wave-numbers in which are given by an equation of the form

$$\bar{\nu}_v = A' + B'n_v' + C'(n_v')^2,$$

where A', B', and C' are constants. Similarly, if n_v' is kept constant, we get a so-called n_v''-progression with a general equation of the form

$$\bar{\nu}_v = A'' + B''n_v'' + C''(n_v'')^2.$$

Both these forms are seen to be that of the DESLANDRES equation given above.

The very satisfactory way in which the wave-numbers of the band origins can be calculated from the above expressions is illustrated in Table XXXIII.

TABLE XXXIII.—WAVE-NUMBERS OF THE BAND ORIGINS OF THE VIOLET CYANOGEN BANDS

$n_v' \rightarrow n_v''$	Observed (cm.$^{-1}$)	Calculated (cm.$^{-1}$)
0–0	25,797·83	25,797·83
0–1	23,755·44	23,755·44
0–2	21,739·54	21,739·55
1–0	27,921·30	27,921·38
1–1	25,879·00	25,878·99
1–2	23,863·00	23,863·10
1–3	21,873·40	21,873·71
2–1	27,962·70	27,962·04
2–2	25,945·50	25,946·15
2–3	22,956·50	23,956·76

Comparing the positions of the band heads, as given in fig. 11, with the quantum transitions given in the first column of Table XXXIII, we see that transitions from a given initial state (i.e. $n_v' =$ constant, say $n_v' = 0$) to different final states (e.g. $n_v'' = 0, 1, 2, 3$) give rise to lines whose distances apart are equal to those between the different groups of bands in the band system. This distance is characteristic of the magnitude of the vibrational quanta. On the other hand, the band origins (or heads) of a particular group of bands are all due to transitions with the same value of $\Delta n_v = n_v' - n_v''$. For example, in the cyanogen system of fig. 11 all the members of the first group on the left have $\Delta n_v = -2$; the members of the second group all have $\Delta n_v = -1$; those of the third all have $\Delta n_v = 0$; those of the fourth all have $\Delta n_v = +1$. Thus the structure of the band groups is an expression of the inequality of spacing of the vibrational levels, i.e. is due to the anharmonicity of the linkage.

5. Electronic Configuration of Molecules

In many band spectra all the lines are found to be double; in some they are all triple. It has been shown that the reason for this lies in the multiplicity of all the energy levels belonging to a given electronic configuration. On the assumption that all the electrons of a molecule form one coherent system, as is the case in an atom, MULLIKEN succeeded in demonstrating analogies in the spectra of molecules and atoms of corresponding structure. Thus the first excited energy level of BeO (and other molecules possessing 9 outer electrons) is double, just as for Na with its 9 electrons outside the K-shell. Moreover, the separation of the components has the value to be anticipated according to p. 312 for a doublet separation due to electron spin. A large number of analogies of this kind have been discovered. Further, a considerable number of different electronic levels have been determined for some molecules, and these have been shown to bear a close relationship to the levels of atoms with similar arrangements of their external electrons. The following are some examples of these analogies. Analogous to the alkali metals (complete shell + 1 electron) are BO, CO^+, CN, and N_2^+, all of which have 13 electrons which may be allotted to shells thus: (2K + 2K) + 8L + 1. The molecule N_2 with 14 electrons [(2K + 2K) + 8L + 2] not only shows the multiplicity of Mg [2K + 8L + 2], but actually has the same component separations (20 cm.$^{-1}$ and about 41 cm.$^{-1}$) as the 2^3P levels of Mg. The molecule CO (14 electrons) is also analogous to Mg. A large number of the electronic energy levels of this molecule are known. Their relationships to the corresponding levels of Mg are shown in fig. 12.

From the above facts we learn that the formation of a molecule from atoms with completed K-shells leaves these shells intact. This is to be expected from considerations of energy; for a very large energy would be required to break into a K-shell. The PAULI exclusion principle (p. 331) states that only two electrons can enter the K-shell, so that in a molecule only two electrons could encircle both nuclei in one-quantum orbits. The other two atomic K-electrons would necessarily be raised to two-quantum orbits. Hence we must conclude that the atoms in the molecule remain surrounded by their own K-shells, whereas (for the light atoms considered above) the incomplete L-shells merge into one another. If this were not so, the above molecules with 13 electrons would not be analogous to Na with its 11 electrons, but to Al with its 13. A direct experimental proof of the intactness of the K-shells in these molecules is also furnished by the X-ray K-spectra, which are practically identical with those of the free atoms.

The second point that emerges is that quantum numbers and vectors, such as were introduced in connexion with atomic spectra, are also applicable to molecules. This is true to a very considerable extent, at least for diatomic molecules. Quantum numbers referring to the electronic structure of molecules are designated by Greek letters corresponding to those used for atoms. Thus λ corresponds to l and Λ to L. The resultant state of the molecule is also symbolized in a similar manner. Thus ${}^1\Sigma$ corresponds to ${}^1S$ and ${}^2\Pi_{3/2}$ to ${}^2P_{3/2}$. Symbols of this kind are given in fig. 12. The quantum number s is still used for the electron spin.

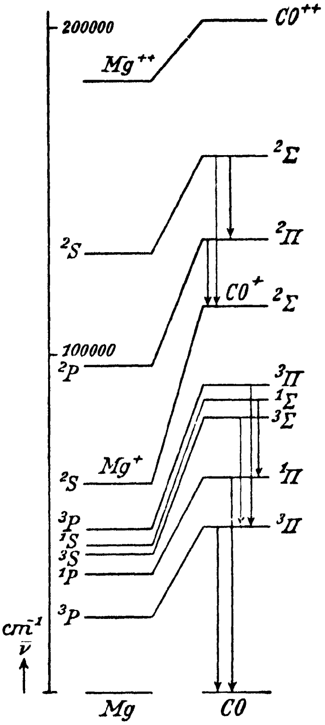

Fig. 12.—Relation between the electronic energy levels of Mg and CO. (The arrows indicate observed transitions.)

When the electronic configuration possesses an angular momentum, it is the *resultant angular momentum* (compounded of the angular momenta of molecular rotation and of the electronic configuration) which is quantized. The electronic contribution includes the electron spins. Several cases may arise with regard to the coupling. For example, λ and s may be very closely coupled, so that they combine to give a quantized resultant i, which then in turn combines with the angular momentum of molecular rotation (here denoted by m) to give the resultant I. Alternatively, the coupling between m and the orbital angular momentum λ of the electrons may be very strong, so that these combine to give a resultant k, which then in turn combines with the spin s to give the resultant I.

Symmetrical Properties and Rotational Structure.—The behaviour of molecules is still further complicated by the non-occurrence of certain transitions between states characterized by special properties of symmetry. Since these peculiarities are of great importance, a very brief account of them may be given here. In the spectra of molecules consisting of two similar atoms, e.g. H_2, a remarkable alternation of intensity is observed in the rotational lines. In the bands of C_2 and O_2 the alternate lines are completely absent (compare fig. 13, p. 382). It has been shown (HUND) that this can be explained by an extension of the PAULI principle to the nuclei (p. 350). It was stated on p. 350 that the nuclei of certain atoms possess an angular momentum or spin. The combination of two like atoms to give a molecule produces a system which is subject as a whole to quantum laws. Hence if, for example, the resultant electronic angular momentum is zero, the molecule can execute only rotations with odd quantum numbers j_r when the two nuclear spins are parallel, and only rotations with even quantum numbers j_r when the two nuclear spins are antiparallel. The quantum-mechanical discussion of this behaviour in the case of H_2 leads to the result that the probability of the parallel orientation of the nuclear spins is three times that of the antiparallel orientation. This is in good agreement with the observation that the intensities of the rotational lines in the band spectrum alternate in the ratio 1 : 3, and with the experimentally determined ratio of ortho-hydrogen to para-hydrogen (p. 352).

B. ROTATIONS AND VIBRATIONS OF MOLECULES AND THE SCATTERING OF LIGHT

6. The Raman Effect

When a strong beam of monochromatic light (e.g. from a mercury vapour lamp) is passed through a liquid (e.g. benzene) which has been very carefully freed from all suspended dust-particles and the like, the light is observed to be scattered in all directions by the molecules of the liquid. This effect is analogous to that referred to in Vol. IV, p. 232 (RAYLEIGH scattering). Its occurrence in the atmosphere accounts for the blue colour of the sky. If the direction of the observation is chosen at right angles to the direction of the primary beam, the scattered light can be investigated independently of the incident light. Spectrographic investigation of the scattering gives lines of the same frequencies as those of the incident spectrum.

In 1928 RAMAN * discovered that the scattered spectrum contains, in addition to the frequencies of the incident spectrum, a number of new frequencies (so-called Raman lines). The effect is shown e.g. in benzene excited by the mercury arc in the visible region. The principal

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* Sir CHANDRASEKHARA VENKATA RAMAN, born 1888, Director of the Indian Institute of Science, Bangalore, and formerly Professor of Physics at Calcutta University. He was knighted in 1929 and received the Nobel Prize in Physics for his discovery of the effect now known by his name.

exciting lines are here the strong blue and violet mercury lines. The Raman lines form a characteristic array on the long-wave side (and more feebly on the short-wave side) of each of these primary lines. If another liquid is taken instead of benzene, the effect is again observed; but now the pattern formed by the Raman lines is different. Thus the Raman effect depends on the chemical nature of the scattering substance. For any particular substance, e.g. benzene, it is found that each primary spectral line gives rise to a set of Raman lines, the *frequency differences* between corresponding Raman lines and their primary lines being always the same, i.e. independent of the frequency of the primary line. These frequency differences or frequency shifts are referred to as *Raman frequencies*. Raman lines corresponding to both negative and positive frequency displacements are observed, the former being the more intense. Thus in the scattering process a portion of the incident light has its original frequency ν_0 either diminished or increased by certain characteristic Raman frequencies ν_R, the frequencies of the Raman lines thus excited being $\nu' = \nu_0 \pm \nu_R$. Now it is found that the Raman frequencies observed in cases like those mentioned above are actually equal to fundamental vibrational frequencies of the scattering molecules. Hence in the excitation of the Raman line of frequency $\nu' = \nu_0 - \nu_R$ we may suppose that the incident light quantum $h\nu_0$ sets the scattering molecule vibrating with the vibrational quantum $h\nu_R$ and is itself scattered with the diminished energy $h(\nu_0 - \nu_R)$. Similarly, the Raman line of enhanced frequency $\nu' = \nu_0 + \nu_R$ is due to scattering by a molecule already vibrating with the energy $h\nu_R$, this energy being given up to the incident light quantum in the process. Thus the Raman effect is to some extent the optical analogue of the Compton effect. The theoretical possibility of such modifications of frequency by molecular scattering had been predicted as early as 1923 by SMEKAL.

The great importance of the Raman effect as a method of investigating molecules lies in the relative simplicity of the technique as compared with that of infra-red measurements and also in the fact that Raman spectra may contain vibrational frequencies which are forbidden in the infra-red. These so-called optically inactive frequencies cannot occur in direct absorption or emission because they are not associated with an alteration of dipole moment and consequently cannot give rise to (or absorb) electromagnetic waves. In the Raman effect, however, they often give the most intense lines.

Rotational energy may also be transferred from the incident light quantum to the molecule (or vice versa) in the scattering process. Since here the energies involved are small relative to the vibrational energies, the pure rotational Raman lines lie correspondingly closer to the primary line. They therefore tend to be masked by the broadening of the much more intense primary line on the photographic plate, and can only be observed in certain cases with refined experimental technique. Two examples are shown in fig. 13.

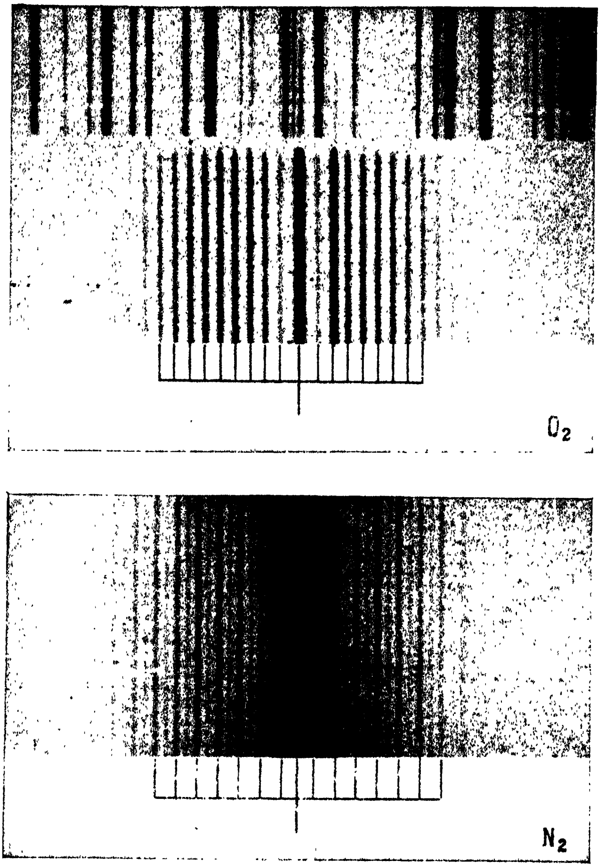

Fig. 13.—Rotational Raman effect in oxygen and nitrogen

[From *Zeitschrift für Physik*, Vol. LXI, 1930 (Springer, Berlin).]

The alternating intensities in the rotational lines of N_2 are clearly visible in the figure. The frequency displacement of the first rotational line is for O_2 larger and for N_2 smaller than the frequency interval between the successive lines. From this we may conclude that only transitions between rotational levels of *odd* quantum number are possible for O_2, and that the stronger lines of N_2 are due to transitions between rotational levels of *even* quantum number (see p. 380).

Transparent solids also give the Raman effect, which thus provides an important method for direct optical investigation of the vibrations of crystals. The effect can also be observed with gases, though here the intensity is correspondingly smaller, owing to the smaller numbers of molecules in a given volume.

The intensity of scattering increases with the fourth power of the frequency (cf. Vol. IV, p. 232) so that, where the absorption of the substance under investigation permits, it is best to use light of as short a wave-length as possible. The ultra-violet mercury resonance line 2537 Å. is often used.

In any case the intensity of the Raman lines is extremely small. This is the reason why the effect was not discovered earlier, in spite of the fact that all the necessary apparatus had long been available and that the effect is quite easy to produce. If a sufficiently intense source is used and the light is concentrated as much as possible, the Raman lines of organic liquids like benzene can actually be made visible.

C. Linkages between Atoms in Molecules

7. Ionic Compounds

Types of Molecules.—The properties of chemical compounds indicate that it is necessary to distinguish between two types of molecules. The first type (e.g. NaCl) forms electrically conducting aqueous solutions in which the molecule is split up into ions (e.g. Na^+ and Cl^-). Even in the solid state, the charges must be distributed unequally between the constituents; for the vibrations of the crystal lattice prove to be optically active (see residual rays, p. 416). Substances of this type usually have relatively high boiling-points and typically salt-like character. They are referred to as **ionic** or **electrovalent compounds.**

The second type includes organic compounds like CH_4 (methane) or C_6H_6 (benzene). These are characterized by their extremely low electrical conductivity, their relative volatility, and their complete lack of salt-like properties. Compounds of this type are referred to as **covalent** or **atomic compounds.**

There are many compounds, however, which cannot be allotted at once to either of the above two classes. More and more criteria are gradually being recognized, but in many cases it is still impossible to say in which class a given compound is to be placed.

Ionic Compounds.—The fact that the individual ions of these compounds can be shown to exist in the solid or liquid states or in solution is evidence for the view that the linkage is electrostatic in character. In the case of NaCl, for example, an electron is transferred from the Na atom to the Cl atom and the resulting ions are held together by electrostatic attraction. It is easily seen that an electron transfer of this kind can only take place when the electron in question is more strongly held by the anion (in spite of the net negative charge) than by the neutral atom from which it was derived. We shall see below that this statement requires considerable modification.

Kossel was the first to remark that the formation of ionic compounds seems to be due to a tendency for atoms to build up complete electron shells or sub-shells, and in particular to assume the configuration of an inert gas. In fig. 14 atomic numbers are plotted as abscissæ and numbers of extra-nuclear electrons as ordinates. The small circles correspond to the neutral atoms, while the black dots correspond to known ions. The positive ions, being formed by loss of electrons, lie beneath their parent atoms. Similarly, the negative ions lie above their parent atoms. The inert gases are indicated by crosses. The figure brings out very clearly the tendency to form ions containing those numbers of electrons (namely 2, 10, 18, &c.) which correspond to completed shells and particularly to the inert-gas configurations. The symbols for the respective electron groups (cf. Table XXVII, pp. 336 to 338) are given on the right of the figure.

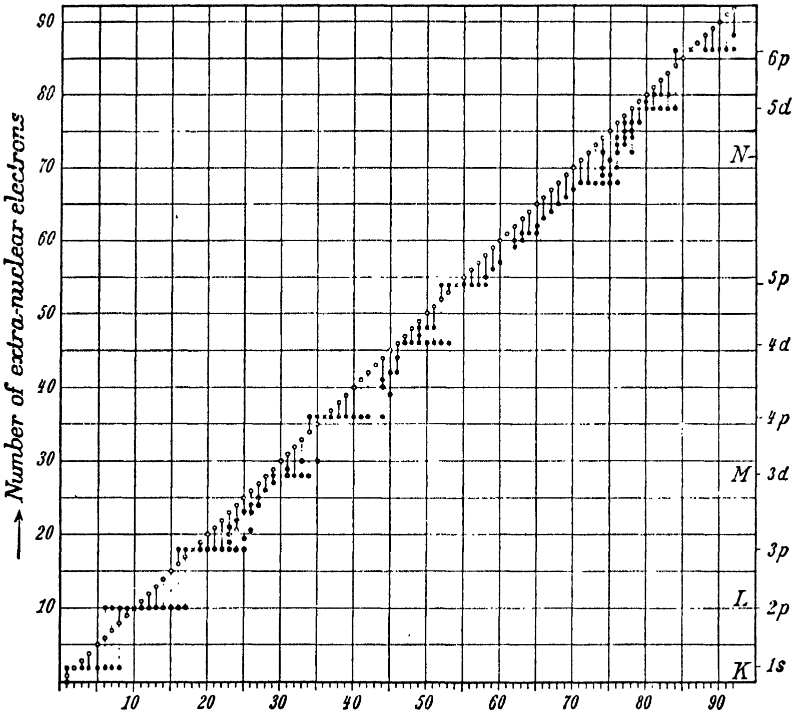

Fig. 14.—Numbers of electrons in observed ions (after Kossel)

Kossel was able to show that the properties of a number of molecules can be accounted for, at least qualitatively, by regarding them as assemblages of spherical ions held together by electrostatic forces. Thus if the series HCl, H_2O, NH_3 is supposed to be ionic, the increasing strength of the linkages from HCl to NH_3 (i.e. the decreasing tendency to split off H^+ in aqueous solution) may be shown to follow from the increase of charge of the negative ion (namely Cl', O'', N'''). This is not immediately obvious, but may be seen from the following simple calculation. Let the negative ion have a charge ze and a radius r_1, and let it be surrounded by z positive ions, each of charge e and radius r_2. The total energy of binding of the whole molecule is then equal to the energy of attraction E_a between the ions minus the energy of repulsion E_r. Assuming that the positive ions are touching the central negative ion, we have

$$E_a = \frac{z^2e^2}{(r_1 + r_2)}.$$

The energy of repulsion cannot be calculated without some assumption as to the arrangement of the positive ions. Assuming that this arrangement has the highest possible symmetry,* we obtain:

$$\text{for } z = 1, \quad E_r = 0;$$

$$\text{for } z = 2, \quad E_r = \frac{e^2}{2(r_1 + r_2)};$$

$$\text{for } z = 3, \quad E_r = \frac{3e^2}{\sqrt{3}(r_1 + r_2)} = \frac{1{\cdot}73e^2}{(r_1 + r_2)}.$$

Hence with the further assumption that $(r_1 + r_2)$ is the same for all three molecules, we obtain the following values for the energy of binding, i.e. for $E = E_a - E_r$: for HCl, $E = e^2/(r_1 + r_2)$; for H_2O, $E = 3{\cdot}5e^2/(r_1 + r_2)$; for NH_3, $E = 7{\cdot}3e^2/(r_1 + r_2)$. The strength of binding may thus be expected to increase in the order HCl, H_2O, NH_3. This is in accordance with the decreasing acid character, i.e. decreasing tendency to dissociate with formation of H^+, which is observed in this order.

The effect of ionic radius may be seen, for example, in the series of molecules H_2O, H_2S, H_2Se, H_2Te. Here the radius of the negative ion increases progressively from O'' to Te'', the actual values being 1·3 Å., 1·7 Å., 1·9 Å., and 2·1 Å. respectively. The strength of binding shows a corresponding progressive decrease, as can be seen from the dissociation constants of the molecules in aqueous solution (10^{-14}, 10^{-7}, 10^{-4}, and 10^{-2} respectively).

As a further example we may take the transition from basic to acidic character within a horizontal period of the periodic table. Fig. 15 is a diagrammatic representation of the attachment of hydroxyl groups OH to the atoms of the period Na to Cl. For the sake of simplicity it is assumed that the positive ions all have approximately the same radius. On account of the small radius of the H^+ ion,

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* An assumption which certainly does not correspond to the actual molecular structures (see Table XXXVI, p. 399).

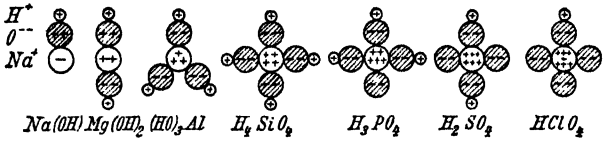


Fig. 15.—The hydroxyl compounds of the elements of the third period of the periodic table (after Kossel)

the attraction between O'' and H^+ in NaOH is greater than that between Na^+ and O''. Hence the compound dissociates in solution to give Na^+ and OH'. The greater the positive charge of the central ion becomes, the more strongly is the O'' held and the greater is the repulsion between the central ion and the H^+. The acid character (i.e. tendency to ionize giving H^+) accordingly increases as we pass through the series of compounds up to $HClO_4$.

Deformation of Ions.—In spite of their qualitative character, the above ideas enable us to summarize a large number of observed facts. Certain refinements, however, are necessary; in particular, the model in which the ions are regarded as rigid spheres can only be a first approximation to the truth. As a second approximation we must take account of the displacements of the outer electron " atmosphere " relative to the positive nucleus which must arise when ions approach one another closely. The existence of such deformations or polarizations of ions can be demonstrated by dipole moment measurements (see Vol. III, p. 104). For example, the distance between the nuclei of the HCl molecule is known from infra-red spectra (p. 366). If we regard this molecule as ionic and assume that the negative charge of the Cl' ion is symmetrically distributed about the Cl nucleus, we should expect the molecule to have a dipole moment of

$$1{\cdot}59 \times 10^{-19} \times 1{\cdot}78 \times 10^{-8} = 2{\cdot}8 \times 10^{-27} \text{ coulomb-cm.}$$

The measured value is only $0{\cdot}46 \times 10^{-27}$ coulomb-cm. Hence if this molecule is regarded as ionic, there must be a very marked displacement of the negative atmosphere of the Cl' ion towards the H^+ ion. This deformation can be calculated and good agreement with experiment is obtained.

Stability of the State of Equilibrium.—The existence of ionic compounds necessarily implies the existence of forces of repulsion between positive and negative ions as the distance between their nuclei is diminished. The occurrence of these repulsive forces makes it possible for the nuclei to take up equilibrium positions of minimum potential energy. The cause of the repulsions may be pictured as follows. Imagine a small positive ion (e.g. H^+) brought towards a negative ion.

As the distance between the nuclei is progressively diminished the positive ion will penetrate into the electron atmosphere of the negative ion. Under these circumstances that part of this electron atmosphere which lies at a greater distance than the positive ion from the nucleus of the negative ion will to a first approximation exert no force on the positive ion, just as a charged hollow metal sphere exerts no force on a charged particle inside it. Hence the force of attraction on the positive ion will be diminished by its penetration into the electron atmosphere of the negative ion. As the distance between the nuclei is further reduced, a position of equilibrium will finally be reached, in which the repulsion between the similarly-charged nuclei is just balanced by the attraction between the positive ion (supposed very small) and the inner region of the electron atmosphere of the negative ion.

8. Covalent Compounds

Molecules like H_2, N_2, Cl_2 cannot be held together by ionic linkages of the kind considered above; for they possess no electric dipole moment, no infra-red absorption, and no tendency to dissociate into ions. Nor can the linkages be effected by the magnetic forces between the atoms, which calculation shows to be too feeble. Some explanation of the linkages appears to be provided, however, by wave-mechanics.

The simplest case is that of the H_2 molecule, which is built up of two nuclei (protons) and two electrons. The structure may be expected to involve the two nuclei, still separate but surrounded by a common electron atmosphere corresponding to the two electrons. The distance between the nuclei can be calculated from the moment of inertia of the molecule obtained from the rotational terms of band spectra, while the rigidity of the linkage (i.e. the restoring force called into play on deformation) can be calculated from the vibrational terms. Finally, the different band systems give information about the possible electronic states.

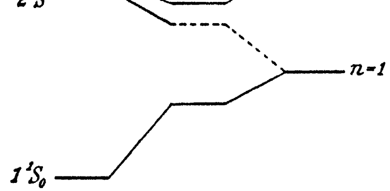


Fig. 16.—Relation between the energy levels of He, H_2, and H (after Hund)

These latter may be expected to show a certain similarity to those of the helium atom; for the H_2 molecule may be imagined to be obtained by dividing the He nucleus into two equal parts and then gradually making these move to the appropriate distance apart. (The difference of mass has only a very small effect.) If the separation is carried still farther, we shall eventually obtain two separate hydrogen atoms. As may be seen from fig. 16, there is in fact a certain relationship between the energy levels in the different cases.

What kind of force is it, then, that links together the two hydrogen atoms in H_2 so strongly that their separation requires an expenditure of about 100 kcal. per gramme-molecule? It cannot be an electrostatic force of the kind which effects the linkages in ionic compounds. The magnetic forces (e.g. those due to electron spin) are too small; indeed the electron orbits of the hydrogen atom in its ground state possess no magnetic moment ($l = 0$).

We may recall that we were faced with a similar difficulty (p. 273) in connexion with the large energy difference between the term-systems of He, which were also inexplicable by the magnetic interaction of the two electrons. In that case we learned that according to HEISENBERG it is the *exchange energy* of wave-mechanical resonance that gives rise to the strong interaction.

Exchange energy of this kind must also be taken into account in the case of the H_2 molecule, which likewise contains two identical electrons. Evidence for the similarity of the two systems is to be found in the relationship between their energy levels. In 1928 HEITLER and LONDON performed the wave-mechanical calculation. They found that the equations give two solutions. As the two hydrogen atoms are gradually brought together the charge distribution around them may assume either the form represented in fig. 17 or that in fig. 18. In the first case the two atoms repel one another at all distances apart, so that a collision between them will be elastic. In the second case (fig. 18) the atoms attract each other at all distances apart down to a certain definite minimum, below which mutual repulsion sets in.

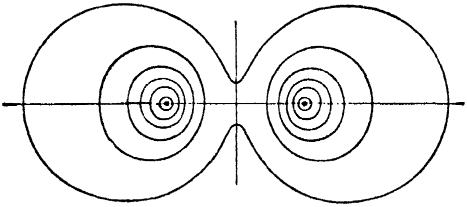


Fig. 17.—Distribution of charge density (lines of equal density) in the electron atmosphere of two mutually-repelling hydrogen atoms.

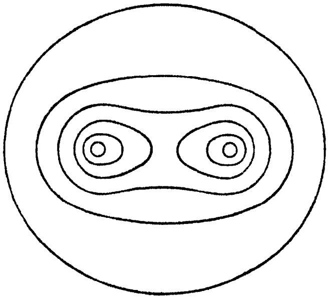


Fig. 18.—Distribution of charge density (lines of equal density) for two hydrogen atoms forming an H_2 molecule.

The variation of the potential energy of the system may be plotted as a function of the distance between the nuclei, the curves of fig. 19

being obtained. The upper curve corresponds to the case represented in fig. 17, in which the potential energy always increases as the distance between the nuclei is diminished. This means that work must be done in bringing the nuclei together. The lower curve corresponds to the case represented in fig. 18. Here the potential energy decreases to a minimum when the nuclei are at the distance d_0 apart. This minimum represents a state of stable equilibrium (actually the ground state of the H_2 molecule). The energy D (see fig. 19) is the energy set free as the distance between the nuclei is diminished from infinity to d_0. Hence this must also be the energy which has to be supplied in order to separate the nuclei of the H_2 molecule completely. Referred to 1 gm.-mol., D is therefore the molecular heat of dissociation. If, as far as is mathematically possible, account is taken of the approximation terms in the problem, satisfactory agreement with observed fact is obtained, the detailed figures being as follows:

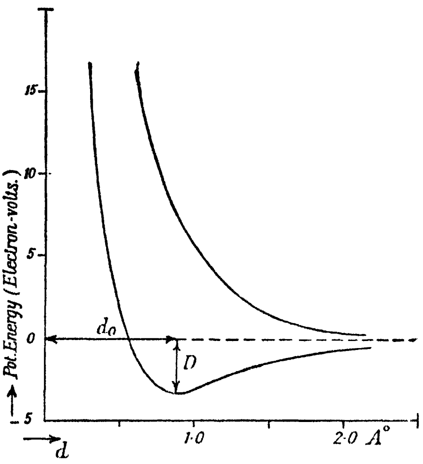


Fig. 19.—Potential energy of two hydrogen atoms as a function of the distance between their nuclei.

	Observed	Calculated
For H_2: Heat of dissociation ..	100 kcal./gm.-mol.	87 kcal./gm.-mol.
Distance between nuclei	0·75 Å.	0·74 Å.

So far it has not been found possible to carry out the calculations for other molecules with sufficient accuracy. The case of H_2, however, indicates the line of approach to an explanation of covalent linkages. Already it is possible to give some account of the valency of atoms in compounds of this kind. The theory, which was first put forward quite empirically by G. N. Lewis, has been extended and given a theoretical basis by the work of London. Lewis pointed out (as Kossel had done for ionic compounds) that the formation of stable covalent linkages (as in CH_4) is accompanied by the completion of electron shells. In N_2, for instance, the strength of the linkage appears to be due to the completion of an L-shell by the electrons from both constituent atoms; for the similarity of the spectrum to that of an alkaline earth (p. 378) indicates that 2 of the 14 electrons are relatively loosely bound and obviously belong to an M-shell. The electrons of N_2 may therefore be arranged in the groups 2K, 2K, 8L, 2M (p. 378). In many cases, however, complete shells appear to be formed around the constituent atoms by the sharing of two electrons, e.g. in Cl_2, C_2H_4, &c. This is especially true of shells of 8 electrons (so-called *octets*). Considerations of this kind make it probable that many linkages (i.e. covalent chemical bonds) are effected by the interaction of two electrons, whose exchange energy holds the atoms in question together in the manner mentioned above for H_2. This is the underlying idea of LONDON's theory. The following considerations render it more precise. As we see from Table XXVI, p. 332, each electronic state (characterized by n, l, and m_l) may be occupied in two ways, the spin of the electron in the one case being opposite to that in the other. Thus a pair of electrons with opposite spins represents complete occupation of any level. This may be expressed by saying that, on account of their opposite spins, the two electrons " neutralize " one another. Actually such an electron pair contributes nothing to the multiplicity r of the level, since their s-values together give zero and according to p. 329 $r = 2\Sigma + 1$. Those electrons which possess no partner in the above sense may obviously become " neutralized " by pairing off with a new electron. It is these unpaired electrons which, according to the theory, are responsible for chemical combination. An atom possesses as many units of valency as it has unpaired electrons. Since the number of these is 2Σ, where Σ is the total spin angular momentum of the atom, the valency of an atom must be one less than the multiplicity of its energy levels. This conclusion makes it possible to test the validity of the theory. As has already been pointed out on p. 329, there is good general agreement with observation: the alkali metals, which have a doublet state as ground state, are univalent; the alkaline earths, which possess a triplet system, are divalent; the trivalent atoms possess a quartet system, and so on. To this extent, then, the theory agrees with fact. It does not agree with fact, however, if we consider the *ground states* of the atoms. Thus the ground state of the alkaline earths is a singlet state, so that according to the theory they should have zero valency, i.e. should exhibit the characteristics of an inert gas. Similarly, the ground state of Al is a doublet state (fig. 7, p. 288), so that Al might be expected to be univalent. Other cases of the same sort may be cited. The multiplicity which is one greater than the valency is first realized in excited states. From this we must conclude that the atoms usually react when in excited states—a conclusion of great importance for an understanding of chemical reactivity, reaction velocity, and the action of catalysts. Since in the excited states the electrons are raised to levels in which the full possibilities of occupation are not realized, increase of excitation is in general accompanied by an increase of valency. Thus, for example, tetravalence in carbon corresponds to an excited state. Variable valency may therefore be expected in the case of atoms (e.g. those of the transitional elements) whose excited states lie relatively close to the ground state. Saturation of the units of valency, i.e. formation of covalent linkages, must manifest itself in the spectrum of the molecule. This is actually found to be the case. For instance, in the combination of N and O to form NO only two electron pairs are formed, one electron remaining without a partner. As is to be expected from the theory, the ground state of NO is found to be a doublet state. The CO molecule, on the other hand, contains no such unpaired electron, and its ground state is accordingly a singlet state. The failure of the theory to account for observed properties in some cases may be exemplified by the strong paramagnetism of O_2 (Vol. III, p. 410). Here all the electrons must be regarded as paired, i.e. " neutralized " in the above sense, and it is therefore difficult to understand why the molecule should possess a magnetic moment. In conclusion we may say that, though we are still far from possessing a complete and quantitative theory of covalent linkages, a line of approach has been discovered which seems to lead in the right direction and is certainly of great importance for the problem of chemical kinetics.

D. THE PROPERTIES OF MOLECULES

9. The Heat of Dissociation

The above theories of molecular structure, together with the theories of atomic structure, throw light on a large number of the properties of molecules, especially the regular variation of properties throughout a series of comparable compounds.

The Heat of Dissociation.—One of the most important quantities characterizing a molecule is the amount of work which must be expended in order to separate the constituent atoms. This is usually expressed in calories and is called the *heat of dissociation* or the *heat of atomization.* It may be calculated from data obtained from the analysis of band spectra. As was pointed out in the discussion of the formation of H_2 (p. 389), the heat of dissociation may be read off from the curve showing the variation of potential energy with distance between the nuclei.

In band spectra where a large number of vibration levels can be distinguished, as is often the case in absorption, the band system is frequently observed to pass over into a region of *continuous* absorption at the short-wave end. An example is shown in fig. 20, which represents the absorption spectrum of iodine in the visible region, the dispersion being relatively small, so that only the band heads corresponding to the successive vibrational levels appear. At the short-wave end the band system is seen to be bounded by a region of continuous absorption. Now the bands are due to the fact that the molecule not only alters its electronic state by the process of absorption, but also its state of vibration (and rotation). The start of the region of continuous absorption indicates that over and above a certain access of vibrational energy, the molecule can take up energy in any quantity. We have encountered similar behaviour in the case of atoms, where a continuum occurs beyond the series limit (p. 194). There the continuum was explained (pp. 194 and 266) by the loss of an electron from the atom when the energy absorbed exceeds a certain amount. Over and above this amount the atom can take up energy continuously, the excess over the energy of ionization being converted into kinetic energy of the electron, which is not subject to quantization. The continuous region of absorption of molecules can be similarly explained. If its vibration becomes too energetic, the molecule will fly to pieces. Above this critical vibrational energy the molecule can absorb continuously, the excess over the energy of dissociation being converted into kinetic energy of the separate atoms, which is not subject to quantization.

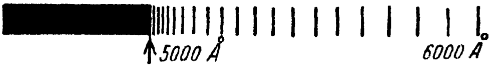


Fig. 20.—Absorption spectrum of I_2, showing continuous region

[From *Handbuch der Experimentalphysik*, Supplementary Vol. I (Akademische Verlagsgesellschaft, Berlin).]

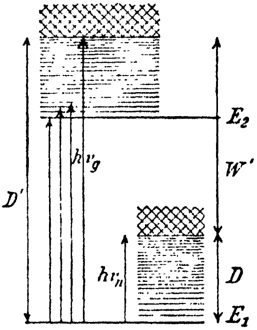


Fig. 21.—Energy levels of the iodine molecule I_2

The interpretation of the data is not always simple, however, because the continuous absorption region is only observed in band spectra whose lines involve an alteration of electronic configuration. An example will make the difficulty clear. Fig. 21 shows the energy level diagram corresponding to fig. 20, only the vibrational levels being shown (i.e. the rotational structure being omitted). The frequency ν_g of the limit of continuous absorption corresponds to the dissociation of the *excited* molecule on account of its energetic vibration. The corresponding limiting frequency ν_n of the normal molecule is not observable in the spectra. Now it is not possible without further information to say what the products of dissociation will be. There are various possibilities (see further p. 394), and it is this ambiguity which constitutes the difficulty of the method. In any particular case it is necessary to investigate the nature of the products of dissociation very carefully. In the case of iodine and many other diatomic molecules (including H_2) the molecule breaks up into one normal atom and one excited atom. The quantity which is of interest from the chemical point of view, however, is the energy or heat of dissociation into two *normal* atoms. To obtain this we must subtract the excitation energy of the one iodine atom from the spectroscopically observed heat of dissociation $D' = h\nu_g$ (see fig. 21). Here again we encounter a difficulty, in that without further investigation we do not know the exact level of excitation concerned. For iodine it is actually the $^2P_{\frac{1}{2}}$ level, the (atomic) excitation energy of which is $W' = 0{\cdot}98$ electron-volt. This is equivalent to 22·6 kcal. per gramme-molecule. Also $\nu_g = 6 \times 10^{14}$ sec.$^{-1}$, so that $h\nu_g = 4 \times 10^{-12}$ erg, which is equivalent to $4 \times 10^{-12} \times 6{\cdot}06 \times 10^{23}$ ergs or 56·8 kcal. per gramme-molecule. The required heat of dissociation into two normal atoms (D) is therefore given by $D = D' - W' = 56{\cdot}8 - 22{\cdot}6 = 34{\cdot}2$ kcal. per gramme-molecule. The value found by thermal experiments is 34·5 kcal. The agreement between the spectroscopic and thermal methods is thus very good. In the case of H_2 the region of continuous absorption is observed to commence at 849·9 Å., the dissociation again giving rise to one excited and one normal atom. The corresponding value of D′ is 334 kcal. The excitation energy of the hydrogen ion can be calculated from the first member of the Lyman series $\lambda = 1216$ Å. (p. 183). The value obtained is $W' = 234$ kcal. The heat of dissociation into two normal atoms is therefore 100 kcal., a value which is in good agreement with that obtained by thermal methods.

An interesting point may be mentioned in connexion with these values. The lines of the band spectra immediately preceding the continuous region are found to be quite sharp. Hence the molecule must be capable of existence for an appreciable time (at least for several vibrations) in the corresponding clearly-defined energy states. The energies possessed by the molecule in these states, however, are often several times the ordinary energy of dissociation D into normal atoms. Thus we see that in certain circumstances molecules may possess amounts of energy considerably higher than those corresponding to their heats of dissociation (cf. fig. 8, p. 371).

As may be seen from fig. 20, p. 392, the vibrational lines (and hence also the vibrational levels) are closer and closer together as we pass towards the region of continuous absorption. Thus in cases where the limit cannot be observed directly (e.g. in emission spectra), its position can be determined approximately by extrapolation. For this purpose the progressive crowding together of the levels is expressed by an equation and the extrapolation is made for the energy at which the interval between successive levels becomes vanishingly small. This method, which has been worked out particularly by BIRGE and SPONER, has also been found to give satisfactory results.

Interest attaches to the occurrence of regions of continuous absorption in the spectra of the vapours of very strongly polar compounds like KCl and NaI, which were considered above as ionic compounds. It has been shown that the long-wave limit of these regions corresponds to those energies which, according to thermal data, are required in order to dissociate the molecules into two *normal* atoms. For KCl, for instance, $\lambda_g = 2800$ Å., so that $h\nu_g = 101$ kcal. per gramme-molecule. The value found by thermal methods is 105 ± 2 kcal. (see Table XXXIV). From this it follows that the continuous absorption is really due to dissociation, and that in the gaseous state absorption of electromagnetic energy causes these molecules to break up, not into ions, but into normal atoms.

Table XXXIV gives a comparison of some heats of dissociation, as determined by the above spectroscopic methods ($D_{\text{opt.}}$) and by thermal methods ($D_{\text{therm.}}$).

TABLE XXXIV

Molecule	$D_{\text{opt.}}$ kcal.	$D_{\text{therm.}}$ kcal.	Molecule	$D_{\text{opt.}}$ kcal.	$D_{\text{therm.}}$ kcal.
H_2	100	95–100	KCl	101	105 ± 2
N_2	220		KBr	91	100 ± 1
Cl_2	58·5	57·2	NaBr	91	90 ± 6
I_2	35·2	34·5	KI	75	84 ± 1
CO	258	(247)			

The Potential Energy Curve.—The general shape of the curve representing the variation of potential energy with distance between the nuclei (see e.g. fig. 19, p. 389, for H_2) can be calculated from the experimentally-determined heat of dissociation and other data obtainable from band spectra. As was pointed out on p. 389, the heat of dissociation gives the height of the asymptote of the curve above the minimum. The distance between the nuclei at the minimum, i.e. in the state of equilibrium, can be calculated from the moment of inertia of the molecule in the state of zero vibrational energy. From the value of ν_0 in the equations of p. 367, i.e. the frequency for harmonic oscillations of small amplitude about the equilibrium position, the curvature of the potential energy curve in the neighbourhood of the minimum may be calculated. For the rate of change of potential energy with distance between the nuclei (i.e. the slope of the tangent to the curve) is equal to the restoring force at the point considered, and ν_0 is proportional to the square root of this force. Other details of the shape of the curve may be deduced from the degree of anharmonicity of the vibrations of greater amplitude, i.e. from the magnitude of x in the equation of p. 367. Further information is obtainable from the change of moment of inertia, which finds expression in the unequal spacing of the rotational energy levels.

Typical examples of potential energy curves for diatomic molecules are shown in figs. 22 and 23, the curves for excited states as well as that for the ground state being given. The shapes shown in fig. 22 are characteristic of covalent molecules like the halogens O_2 and H_2. The molecule is very stable in the ground state, but electronic excitation is accompanied by a loosening of the linkage, i.e. by a diminution of the heat of dissociation. Fig. 23 shows the opposite case, in which the linkage is strengthened by electronic excitation (i.e. by an increase of the average distance of the electrons from the nuclei). This chemically interesting behaviour is shown only by molecules (e.g. NO, HgH) which have a doublet band spectrum. According to p. 391, this type of spectrum indicates the presence of an unpaired electron, which thus seems to weaken the chemical linkage.

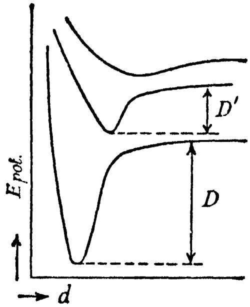


Fig. 22.—Potential energy curves of diatomic molecules (H_2, O_2, and halogens).

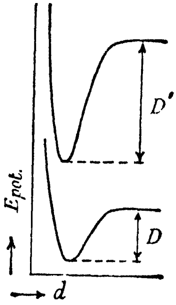


Fig. 23.—Potential energy curves of diatomic molecules (NO, HgH, &c.).

10. The Size and Shape of Molecules

In the last few years the combination of results obtained by the most varied methods has yielded detailed information as to the size and shape of molecules. It is now possible to determine, not only the relative positions of the nuclei, but also the forces acting between them, the nature of their characteristic vibrations, and the distribution of electric charge in the molecule.

In the first place, the kinetic theory of gases gives the approximate sizes of molecules, the number of their degrees of freedom, and similar general information. Chemical methods supply a large number of more detailed features. The most

precise results, however, have been obtained to a large extent from the investigation of electrical and optical properties. Band spectra give information about the vibrations and rotations of molecules and hence, as was shown above (p. 391 *et seq.*), about distances between nuclei, moments of inertia, heats of dissociation, &c., as well as about the possible electronic states. The spectra of scattered light (Raman spectra) provide important complementary information. From the diffraction effects observed when a beam of X-rays or electrons is passed through a gas (fig. 30, p. 251) it is possible to calculate the distances between the atoms in the molecule, while conclusions as to the distribution of the electric charges can be drawn from investigations of the dielectric constant (Vol. III, p. 104) or of the Kerr effect (Vol. IV, p. 257). The following is a short account of the results obtained by these methods.

The kinetic theory of gases gives the distances up to which molecules can approach one another in ordinary thermal collisions. There are various ways in which this quantity can be derived. The viscosity η and the molecular diameter d are connected by the equation

$$d^2 = 4{\cdot}56 \times 10^{-20} \frac{\sqrt{M}}{\eta(1+C)},$$

in which M is the molecular weight and C is a constant (lying between 50 and 300) which is introduced in order to allow for the mutual forces of attraction between the molecules. A value of d can also be obtained from the constant b of the van der Waals equation, using the relation

$$b = \frac{2\pi}{3} N d^3,$$

where N is Avogadro's number. Conclusions as to the size of molecules can also be drawn from the distances between the molecules in the solid state, as determined by X-ray diffraction. The radius r of molecules in the liquid state can be estimated from determinations of the molar volume V at very low temperatures. Assuming the molecules to be spherical and to be packed together as closely as possible, we have

$$\frac{4\pi r^3}{3} = \frac{0{\cdot}74V}{N}.$$

These different methods all give values of the order of a few Ångström units. The values obtained for He, for instance, are: from η, 1·96 Å.; from V, 4·0 Å.; and from b, 2·5 Å. The corresponding values for O_2 are: 3·0 Å.; 3·9 Å.; and 2·6 Å. For CO_2: 3·3 Å.; 4·6 Å.; and 3·2 Å. Another method is available for substances which can be spread in layers one molecule thick on the surface of water. Measurement of the weight and area of the film gives the area occupied by each molecule. The values obtained for d, the molecular diameter, are again a few Ångström units.

A further important question is that of the distances between the atoms within the molecule. These can be determined from the diffraction of X-rays or electrons by the molecules in the vapour state (fig. 30, p. 251). Very accurate measurements have been made upon the molecule CCl_4, in which all four Cl atoms are the same distance from the central C atom. The results given by the two methods for the distance Cl — Cl between chlorine atoms are respectively 2·99 ± 0·03 and 2·98 ± 0·03 Å. The value for C — Cl is found to be 1·82 Å. A large number of compounds have been investigated. An account of the determination of molecular moments of inertia by optical methods has already been given (p. 365). Here the measurements are made on the rotational structure of band spectra or Raman spectra (see e.g. fig. 13, p. 382). Consideration of the results of all these investigations for a very large number of organic molecules leads to the result that the length of any particular chemical linkage (e.g. C = C) is very nearly independent of the rest of the molecule in which it occurs. Indeed it is possible to ascribe to each atom a definite effective radius in each type of combination. Thus in organic molecules we have the following values: H—, 0·3 Å.; C—, 0·77 Å.; C=, 0·65 Å.; C≡, 0·58 Å.; N—, 0·7 Å.; N=, 0·63 Å.; N≡, 0·55 Å.; &c. From the experimental data conclusions may be drawn as to the *shape* of the molecule under consideration—whether it is straight or bent, and so on. The tetrahedral arrangement of the four valencies of carbon, postulated empirically by the chemists, has been verified in many instances.

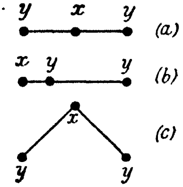


Fig. 24.—Possible shapes of the triatomic molecule XY_2.

Another important method of investigation is the determination of electrical dipole moments (see Vol. III, Table II, p. 104). The number of compounds (especially organic compounds) which have been examined in this way is very large. Almost all diatomic molecules with two similar atoms (e.g. N_2, O_2, I_2) possess no permanent dipole moment, whereas molecules with unlike atoms (e.g. HCl, CO, NO) possess large moments, i.e. markedly unsymmetrical charge distributions. Closer examination of the results shows that a definite dipole moment may be ascribed to each linkage between two atoms (e.g. C — H, O — H, &c.), even in complicated molecules. In the case of triatomic molecules of the type XY_2 it is possible to deduce whether the shape (fig. 24) is (*a*) straight and symmetrical, (*b*) straight and unsymmetrical, or (*c*) bent. Thus the absence of an electrical dipole moment for CO_2, CS_2, $HgCl_2$, $HgBr_2$, HgI_2 indicates that in the gaseous state all these molecules have the straight symmetrical form. In order to discriminate between cases (*b*) and (*c*) of fig. 24 other methods must be used which permit of deductions as to the type of symmetry of the molecules. Such methods are the very difficult analysis of the vibrational states of band spectra and the number and state of polarization of the Raman lines. The molecules H_2O, H_2S, and SO_2 have been shown to have the bent shape of fig. 24 (*c*), while N_2O has the unsymmetrical shape of fig. 24 (*b*).

From the degree of polarization of coherently scattered light (Tyndall effect or Rayleigh scattering, Vol. IV, p. 232) conclusions can also be drawn as to the variation of the polarizability of the molecules in different directions (optical anisotropy). In the scattering process the " electron atmosphere " of the molecule is caused to oscillate with the frequency of the incident light. If now the electron atmosphere is not equally polarizable in all directions, its oscillations will not always be in the same direction as those of the electric vector of the incident light, and as a result the scattered light will be partially depolarized.

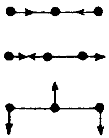
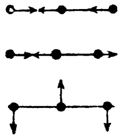
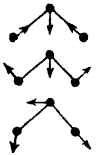
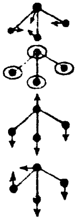
Another very important method of investigation depends on the Kerr effect (KERR, 1875, see Vol. IV, p. 257), i.e. the appearance of double refraction (different velocities of light in different directions) when an ordinarily isotropic substance is placed in an electric field. The effect is mainly due to the partial orientation of the molecules in the field, with the result that the oscillations of the electron atmospheres under the influence of light become different in the longitudinal and transverse directions. From observations of this kind, as from observations upon light scattering, it is possible to determine the anisotropy of the electrical polarization of the molecules.

An enormous mass of data has already been accumulated by the methods mentioned above. Some of the results, as collected by STUART, are given in Tables XXXV and XXXVI.

TABLE XXXV.—DATA FOR DIATOMIC MOLECULES

	Molecule				
	H_2	O_2	Cl_2	HCl	
Internuclear distance	0·75	1·20	1·98	1·28	$\times 10^{-8}$ cm.
Moment of inertia	0·47	19·2	113·7	2·61	$\times 10^{-40}$ gm. cm.^{2}
Gas-kinetic diameter	2·8	3·2	4	3·5	$\times 10^{-8}$ cm.
Nuclear vibration frequency ν	12·8	4·7	1·68	8·3	$\times 10^{13}$ sec.$^{-1}$
$\bar{\nu}$	4264	1577	560	2780	cm.$^{-1}$
Energy of dissociation	4·4	5·1	2·47	4·4	electron-volts
Electric dipole moment	0	0	0	0·24	$\times 10^{-8}$ *e*-cm.

TABLE XXXVI.—DATA FOR TRIATOMIC AND TETRATOMIC MOLECULES

	Molecule				
	CO_2	N_2O	H_2O	NH_3	
Shape	straight symmetrical	straight unsymmetrical	bent angle = 105°	symmetrical pyramid	
Nuclear distances	C – O : 1·15	—	O – H : 1·0 H – H : 1·5	N – H : 1·04 H – H : 1·75 height : 0·3	$\times 10^{-8}$ cm.
Moment of inertia	70·2	66·0	0·995 1·9 2·98	2·8 2·8 4·4	$\times 10^{-40}$ gm. cm.^{2}
Gas-kinetic diameter	3·3	3·2	2·7		$\times 10^{-8}$ cm.
Electric dipole moment	0	0·03	0·38	0·31	$e \times 10^{-8}$ cm.
		N N O			
Proper vibrations ν_1 ν_2 ν_3 ν_4					
$\bar{\nu}_1$	1322	1285	(3600)	964·3 and 933·8	cm.$^{-1}$
$\bar{\nu}_2$	2363	2224	1595	1630 and 1630	
$\bar{\nu}_3$ $\bar{\nu}_4$	668	589	3756	3336, 3300 and 3300	

Regularities of Internuclear Distances.—When plotted against atomic number, the distances between the nuclei in the hydrides show a remarkable periodicity (see fig. 25), the separate parts of the graph being nearly linear. We see that the internuclear distance suddenly becomes larger where, according to the theory of atomic structure, an electron shell or sub-group has been completed and a new shell is being started. Since the one atom (here H) remains the same throughout, these increases of internuclear distance indicate that the linkage is in each case effected by an electron belonging to a shell outside the completed shells of the preceding inert gas.

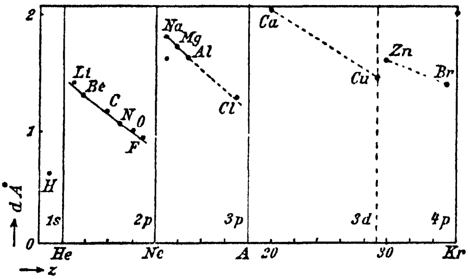


Fig. 25.—Internuclear distances in hydrides

CHAPTER VII

The Structure of Solids and Liquids

1. The Forces which hold Molecules together

At sufficiently low temperatures all gases liquefy or solidify, the molecules attracting one another and clustering together into a definite volume. The molecules must also be capable of repelling one another; for very high pressures are necessary to compress liquids or solids, i.e. to diminish the distances between the molecules. The variation of force with distance must therefore have the form shown in fig. 1. The repulsion at small distances apart increases much more rapidly as this distance decreases (in many crystals proportionally to about the ninth power—see p. 409) than the attraction which predominates at greater distances does.

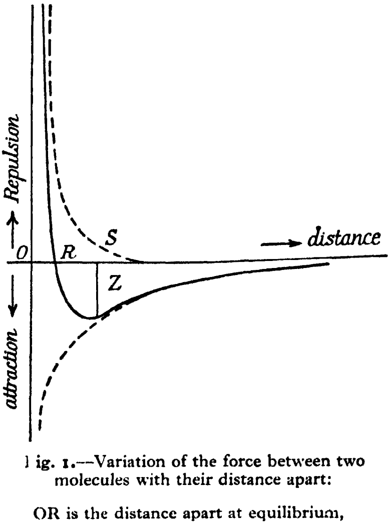


Fig. 1.—Variation of the force between two molecules with their distance apart:

OR is the distance apart at equilibrium,
Z the theoretical breaking stress,
S the repulsion curve by itself.

Origin of the Forces of Attraction and Repulsion.—These forces are undoubtedly electric and magnetic in character. We know that many molecules possess permanent electric dipole moments or have such dipole moments induced in them by the internal fields of the bodies of which they form a part. Now a dipole exerts a force of attraction proportional to $1/r^3$ (Vol. III, p. 100) in the direction of its axis. In the plane at right angles to the axis and passing through its middle point the force is zero. For less markedly asymmetrical charge distributions the force of attraction falls off more rapidly as the distance increases, e.g. for a quadrupole proportionally to $1/r^4$. Hence dipoles have a tendency to hold together as shown in fig. 2. A number of compounds are known to exist in the form of double molecules or more highly associated molecules even in the gaseous state (e.g. acetic acid — double molecules). The cohesion of molecules in the solid or liquid state, however, appears to be largely due to intrinsically feebler dipole moments induced by the intense interactions occurring at small distances of separation. Those substances (e.g. water) whose molecules possess large permanent dipole moments even in the gaseous state, show additional complications (formation of association complexes) in the liquid and solid states.

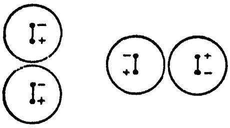


Fig. 2.—Association of dipoles

The forces of repulsion which come into action at very small distances of separation may be regarded as mainly due to the mutual repulsion between the similarly charged nuclei. The way in which this repulsion increases in effect as a small positive particle (positive ion or positive nucleus) penetrates into the electron atmosphere of an atom (or molecule) has already been discussed on p. 87.

Ionic lattices (e.g. crystalline NaCl) form an extreme case of the holding together of a solid by electrostatic forces. Here the molecule loses its individuality altogether, each ion being surrounded by an equal number of neighbouring ions of the opposite kind, which in many cases all bear the same relationship to it. Thus in crystalline NaCl (rock salt) each Na^+ ion is surrounded symmetrically by six Cl' ions and each Cl' ion by six Na^+ ions (see Vol. I, fig. 18, p. 276).

As a result of the regular structure of lattices of this kind, in which the atoms preserve a certain individuality, all these so-called *simple solids* exhibit marked general regularities in their behaviour. Over a wide range (to a specific heat of $C_v = 0{\cdot}3$ cal. per gramme) they have a heat content U which is proportional to T^4, so that the specific heat is proportional to T^3. Again, the volume or linear expansion between two temperatures is proportional to the corresponding change of internal energy, i.e. the coefficient of thermal expansion is proportional to the specific heat.

Thermal Expansion.—In solids the atoms in general occupy certain positions of equilibrium, about which they may perform oscillations but from which they cannot migrate.

The change of position of atoms in solids has been investigated in certain cases by means of radioactive isotopes (e.g. lead), whose progress through the main bulk of the solid may be detected. Experiments of this kind have shown that a slow exchange of places between atoms (self-diffusion) occurs even in solids. This, however, is very slow, especially at low temperatures.

The equilibrium position corresponds to the point R of the force curve of fig. 1, p. 401. Since the slope of the curve is not the same on both sides of this point, a greater force is required to diminish the distance of separation (i.e. the abscissa) by a certain amount than to increase it by the same amount. Hence the oscillations of the molecules about the equilibrium position must be asymmetrical, and as the amplitude of oscillation increases (i.e. as the temperature rises) the mean position will move farther and farther to the right in the figure. Macroscopically this is observed as an expansion of the body. Thus *the expansion of a solid is due to the asymmetry of the potential energy curve.*

The Melting Process.—As the amplitude of oscillation becomes greater and greater, the individual atoms or molecules eventually " collide " with one another, i.e. approach so close to one another that their interactions prevent them returning to their original equilibrium positions. When this happens for a sufficiently large number of atoms or molecules, the whole crystal structure breaks down and the solid melts. In this connexion it is a remarkable fact (GRÜNEISEN) that all simple solids expand by about 1/13 in the temperature range from the absolute zero to the melting-point (which is very different in different cases).

2. Crystals

Structure of Solids.—Solids are characterized by their elasticity of volume and shape, i.e. they possess a definite volume and shape which return to their original values on the removal of deforming forces. Solids may be either crystalline or amorphous (Vol. I, p. 269). Amorphous bodies, such as glasses, may be regarded as liquids of very high viscosity. In the case of crystalline bodies it is necessary to differentiate between those which have a completely regular structure throughout (single crystals) and those which consist of an assemblage of a very large number of crystalline fragments in random orientation (microcrystalline or polycrystalline bodies). The single crystal may be regarded as the ideal solid.

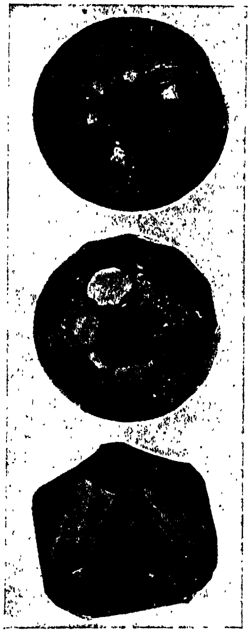


Fig. 3.—Development of faces in the growth of a crystal of chrome alum from a sphere (after Gunther).

From *Die Naturwissenschaften* (1930) (Springer, Berlin).]

As a rule a homogeneous non-crystalline substance is isotropic, i.e. its properties (such as refractive index for light, velocity of propagation of sound, thermal and electrical conductivities, &c.) are independent of the direction in which the light, sound, heat, or electric current passes through. Crystals, on the other hand, are anisotropic, i.e.

their physical properties are different in different directions. There is a definite direction in a crystal in which the physical properties have maximum or minimum values. A flake of graphite, for example, has an electrical conductivity along its plane which is 100 times that in a direction normal to its plane. In a cubic crystal of rock salt the velocity of sound parallel to a diagonal of the cube is 15 per cent less than that parallel to an edge (cf. also Vol. I, fig. 2, p. 198). Amorphous and crystalline bodies also differ in their behaviour towards a solvent. A sphere of glass immersed in hydrofluoric acid remains spherical as it dissolves; but a single crystal (e.g. of NaCl), when ground into a sphere and suspended either in water or in saturated salt solution, develops characteristic facets as it dissolves or as more salt crystallizes out on it (fig. 3).

Most crystalline bodies are polycrystalline. Only a few minerals occur naturally in perfectly formed single crystals suitable for investigation. Various methods have been devised for the preparation of single crystals. Large crystals of salts may be deposited from saturated solutions under suitable conditions. Small added crystals, which act as nuclei for deposition, can often be left to grow. In most cases, however, there is an upper limit to the size of the single crystals which can be prepared in this way. Larger crystals are obtained by placing a small single crystal in a certain orientation in the molten substance. It is possible to arrange for the whole melt to solidify to a single crystal with the orientation of the added nucleus. In another method an added single crystal is withdrawn from the melt at a certain velocity, so chosen that the deposition of the solid upon it gives a large crystalline mass. In this way single crystals weighing several kilograms may be prepared. Polycrystalline wires may suddenly pass over into more or less large single crystals when loaded almost to the breaking-point. If the load is too great, the planes of the single crystals glide over one another in the manner illustrated for a single crystal of cadmium in Vol. I, fig. 17, p. 210. This gliding is favoured by high temperature. Imperfect crystals may be rendered more nearly perfect by annealing (maintenance at a definite temperature) and slow cooling (see Vol. I, figs. 7, 8, and 9, pp. 269 and 270).

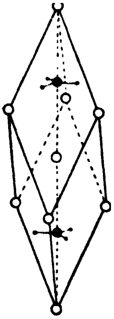
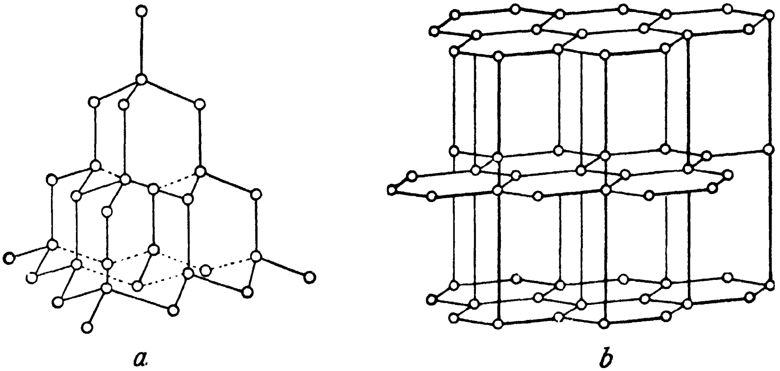


Fig 4.—Lattice structure of calcite($CaCO_3$).

○ = Ca
● = C
• = O

Crystal Structure.—The regular external shapes of crystals and the differences of properties in different directions are evidence of a perfectly regular internal structure. The diffraction of X-rays and electrons by crystals (pp. 63 and 243 respectively) proves that the structure consists of a regular lattice of diffracting centres. The lattice spacings can be determined by means of the Bragg relationship (p. 68). Information as to the *nature* of the diffracting centres is obtainable from the intensities of the diffracted beams. The distribution of intensity in the diffraction pattern also throws light on the arrangement of the different centres within the space lattice. In the case of salts which are strong electrolytes it has been found that the lattice points are the ions (*ionic lattice*). Thus NaCl has a cubic lattice consisting of Na$^+$ and Cl$'$ ions (see Vol. I, fig. 18, p. 276). Polyatomic ions



(*a*) Diamond (linkages of the aliphatic type)

(*b*) Graphite (linkages of the aromatic type)

Fig. 5.—Lattice structures of carbon

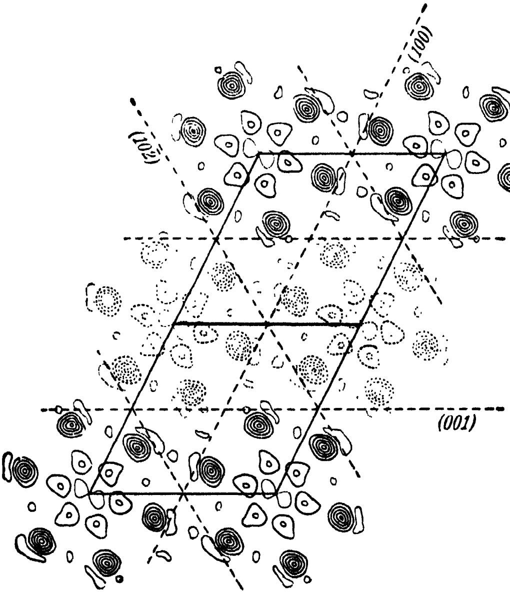


Fig. 6.—Contours showing the distribution of electric charge-density in crystalline hexachlorbenzene C_6Cl_6 (after Lonsdale). The dotted contours refer to a plane lying below that of the figure. Four C_6Cl_6 molecules are represented in the main plane of the figure. In each of these are seen 6 markedly deformed C atoms surrounded by 6 less deformed Cl atoms.

[From *Proc. Roy. Soc.*, A., Vol. CXXXIII (1931).]

like NO_3' and CO_3' are built into crystal lattices as distinct units (see fig. 4). In certain cases a more or less well-defined grouping of certain atoms occupying lattice positions may be recognized (molecular lattices, Vol. I, p. 276). Special interest attaches to those lattices in which the atoms are arranged in *layers*, the forces holding the different layers together being much smaller than those holding together the atoms in any one layer. An example of this is graphite (fig. 5*b*), the properties of which are in strong contrast to those of diamond (fig. 5*a*, non-layer type of lattice). Fig. 6 shows the extent to which information can be obtained about the distribution of electric charge-density in particular cases.

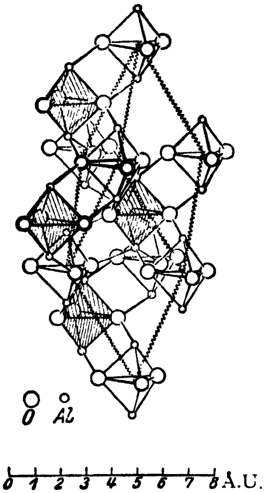


Fig. 7.—Unit cell of corundum (Al_2O_3)

[From *Handbuch der Physik*, Vol. XXIII, Part 2 (Springer, Berlin).]

A crystal lattice may be thought of as built up by the arrangement of unit cells side by side (fig. 7) or by the piling up of parallel lattice planes. In a simple cubic lattice, for example, the unit cell is itself cubic (see Vol. I, fig. 17, p. 275), having atoms at each corner and also in many cases an atom at the centre of the cube (body-centred lattice) or at the centre of each of the cube faces (face-centred lattice). See fig. 8.

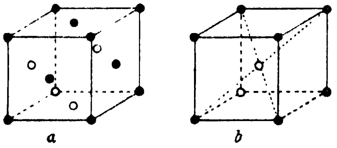


Fig. 8.—Cubic lattices: (*a*) face-centred and (*b*) body-centred.

In the KCl crystal the Cl' ions alone and the K^+ ions alone each form a face-centred cubic lattice. The same is true of the halides of Li, Na, K, and Rb. The simple cubic lattice, built up of only one kind of particle, does not occur in nature, but many body-centred cubic lattices are known. This latter type may be considered as derived from the interpenetration of two simple cubic lattices, the corners of the one occupying the body-centres of the other. This is the kind of lattice in which CsCl, CsBr, CsI, TlCl, and the halides of NH_4 crystallize, the positive ions in each case forming one simple cubic lattice and the negative ions the other. The metals Li, Na, K, V, Cr, Mo, W, Fe_α, and Ta also crystallize in body-centred lattices, all the lattice points being here occupied by atoms of the same kind. Some metals, e.g. Cu, Ag, Au, Ca, Pb, Fe at high temperatures, Fe_γ, Al, Pd, and Pt, crystallize in face-centred cubic lattices.

For some compounds, and especially for metals, the crystal structure depends on the temperature. Different solid phases exist in definite temperature ranges. Thus in the case of iron it is possible to differentiate between α-, β-, γ-, and δ-phases. At lower temperatures the stable form of iron is the α-phase (body-centred cubic lattice), at higher temperatures the γ-phase (face-centred cubic lattice).

Table XXXVII (after Grimm) gives the interionic distances in the alkali halide lattices of the NaCl type (mostly determined by X-ray diffraction). The Δ-values also included in the table are the differences for pairs of corresponding salts. We see that the interionic distance increases when a lighter anion or cation is replaced by a heavier. This suggests that a definite size (or rather a definite sphere of action) may be ascribed to each ion, the distance between a pair of ions in a lattice being obtained by simply adding their effective radii.

Table XXXVII.—Interionic Distances (in Å.U.) in the Alkali Halides

	F	Δ	Cl	Δ	Br	Δ	I
Li	2·02	(0·55)	(2·57)	0·175	(2·745)	(0·265)	3·01
Δ	0·32		(0·25)		(0·265)		0·24
Na	2·34	0·48	2·821	0·19	3·01	0·24	3·25
Δ	0·35		0·31		0·29		0·30
K	2·69	0·44	3·13	0·17	3·30	0·25	3·55
Δ	(0·19)		(0·16)		0·165		(0·15)
Rb	(2·88)	(0·41)	(3·29)	(0·175)	3·465	(0·235)	(3·70)

On this view crystals may be regarded as built up by the closest possible packing together of spheres. The distances between the lattice points can then be calculated from the molar volume. The bracketed values in Table XXXVII were obtained in this way. The occurrence of different crystal forms can also be understood in terms of the packing together of spherical atoms. As has been shown in particular by Goldschmidt, a large number of observed facts can be explained in this way. Fig. 9 illustrates, by a two-dimensional example, how the relative sizes of the units may affect the way in which they pack together. Here the arrangement shown on the left, in which the smaller unit is surrounded by *three* larger neighbours, is possible up to the ratio of radii 0·41 : 1. When the packing is in space, four neighbours are

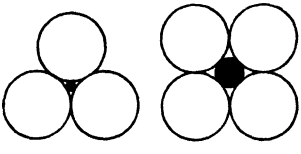


Fig. 9.—Effect of the relative sizes of ions on the type of packing

possible (tetrahedral configuration, as in ZnS) up to the ratio of radii 0·41 : 1. Then the arrangement with six neighbours is stable up to the ratio 0·73 : 1 (rock-salt lattice type). Thereafter an arrangement with eight neighbours becomes stable, the units occupying the corner points of two interpenetrating cubic lattices (CsCl type). The assumption that the lattice distances in crystals are simply the sums of the effective radii of the ions concerned holds fairly well for the alkali halides; but for other salts it is less satisfactory, on account of the effects of the ions upon the charge distribution of their neighbours (polarization and deformation). The effective sizes of the ions, as calculated from their distances apart in crystals, are not completely filled by the ions. The determination of the "true" ionic magnitudes presents many difficulties. A satisfactory estimate can only be made for ionic compounds, in which the forces between the ions are more amenable to discussion. Table XXXVIII gives some ionic radii as

TABLE XXXVIII.—IONIC RADII IN Å.U.

Group							Group		
VI$_A$	VII$_A$	O	I$_A$	II$_{AB}$	III$_{AB}$	IV$_{AB}$	I$_B$	II$_B$	III$_B$
O″ 1·3	F′ 1·3	Ne 1·17	Na· 0·98	Mg·· 0·7	Al··· 0·55	Si···· 0·4			
S″ 1·8	Cl′ 1·8	A 1·4	K· 1·3	Ca·· 1·0	Sc··· 0·8	Ti···· 0·65	Cu· 0·96	Zn·· 0·8	Ga··· 0·6
Se″ 1·95	Br′ 1·95	Kr 1·6	Rb· 1·48	Sr·· 1·2	Y··· 1·0	Zr···· 0·85	Ag· 1·2	Cd·· 1·0	In··· 0·85
Te″ 2·2	I′ 2·2	Xe 1·75	Cs· 1·65	Ba·· 1·4	La··· 1·2	Ce···· 1·0	Au· 1·4	Hg·· 1·1	Tl··· 1·0

deduced from interionic distances in crystals and from wave-mechanical considerations. All the ions in a horizontal row have the same number of extranuclear electrons. Within such a row the ionic radius decreases as the nuclear charge increases. This is to be expected; for an increase of nuclear charge means a greater attraction between the nucleus and the surrounding electron atmosphere. Comparison of the ions in a vertical column shows that the radius increases as the element becomes heavier. This is due to the extra electron shells of the heavier atoms.

In order to arrive at a more detailed theory of how the atoms in crystals are held together, we must be clear about the forces which are acting. From the regularity and permanence of the arrangement of the crystal units, it is clear that these must be in equilibrium. Two ions at a relatively large distance apart act on one another like point charges, i.e. they attract one another or repel one another according as they are oppositely or similarly charged. At smaller distances apart, however, two oppositely charged ions must repel one another; otherwise there could be no position of equilibrium at a definite distance apart. The force F between two oppositely charged ions of charges e_1 and e_2 at a distance r apart may therefore be written in the form

$$F = \frac{e_1 e_2}{r^2} - \frac{b}{r^m},$$

where b and m are constants. The first term represents the Coulomb attraction, while the second (of opposite sign) represents a repulsion. The index m is large in comparison with 2, so that for small values of r the repulsion overcomes the attraction. Wave-mechanics offers the possibility of calculating the potential energy of two ions at these small distances apart, without any special assumptions concerning the forces of repulsion.

If the ionic radii in a lattice are known, the lattice energy can be calculated in simple cases. By lattice energy we mean the work which would have to be done in order to break down 1 gm.-mol. of the crystal completely into 1 gm.-atom of gaseous positive ions and 1 gm.-atom of gaseous negative ions. In the gaseous state the ions are supposed to be very far apart. Using the above equation for the force between two ions, we can calculate the potential energy of the whole lattice by summing the contributions due to each pair of ions. The calculation is difficult and can only be performed in simple cases. It is simplified by the introduction of the so-called MADELUNG summation factor α, which has a definite value for each type of lattice, depending upon the spatial arrangement of the ions as determinable by X-ray analysis. If we regard the ions as perfectly rigid spheres, the lattice energy is given by the equation

$$L = \frac{N z^2 e^2 \alpha}{r_1 + r_2},$$

in which N is Avogadro's number, z the number of charges on the ion of lower valency (e.g. $z = 1$ in $CaCl_2$ and $z = 2$ in CaO), e the elementary charge, and r_1 and r_2 the respective ionic radii. BORN modified the calculation by taking into account the deformabilities of the ions. He then obtained the expression

$$L = \frac{N z^2 e^2 \alpha}{r_1 + r_2}\left(1 - \frac{1}{n}\right),$$

in which n is the index in the expression for the potential due to the forces of repulsion. For crystals of the NaCl type $n = 9$.

These theories may be compared with observation by considering the following cyclic process for NaCl (Born and Haber). A gramme-molecule of the crystalline salt may be imagined to be formed either directly from one gramme-atom of solid sodium and half a gramme-molecule of gaseous chlorine,* in which case the heat of formation B is set free, or alternatively by the following processes:

$$\begin{tikzcd}
{[\mathrm{Na}] + (\tfrac{1}{2}\mathrm{Cl}_2)} \arrow[rr, dashed, "-S_{\mathrm{Na}} - \frac{1}{2}D_{\mathrm{Cl}_2}"] \arrow[d, "+B"] & & {(\mathrm{Na}) + (\mathrm{Cl})} \arrow[d, "-I_{\mathrm{Na}}"', "+E_{\mathrm{Cl}}"] \\
\begin{array}{c}[\mathrm{NaCl}] \\ \text{crystal}\end{array} & & {(\mathrm{Na}^+) + (\mathrm{Cl}^-)} \arrow[ll, "+L_{\mathrm{NaCl}}"'] \arrow[dl, "+V_{\mathrm{NaCl}}"] \\
& \begin{array}{c}(\mathrm{NaCl}) \\ \text{vapour}\end{array} \arrow[ul, "+S_{\mathrm{NaCl}}"] &
\end{tikzcd}$$

(1) The solid sodium is vaporized so as to give sodium atoms, and the chlorine is dissociated so as to give chlorine atoms. This step requires the supply of the gramme-atomic heat of sublimation (S_{Na}) of sodium and half the gramme-molecular heat of dissociation ($\frac{1}{2}D_{\mathrm{Cl}_2}$) of chlorine.

(2) The sodium atoms thus obtained are ionized, the electrons removed from them being transferred to the chlorine atoms to give chlorine ions. This step requires the supply of the energy of ionization (I_{Na}) of a gramme-atom of sodium and the liberation of the energy E_{Cl} corresponding to the electron affinity of the chlorine.

(3) The crystal lattice may now be built up directly from the Na^+ and Cl^- ions, the lattice energy L_{NaCl} being thereby set free. Alternatively, the ions may be allowed to combine in pairs to give NaCl molecules (a process in which the heat of formation V_{NaCl} of NaCl from its ions is liberated), and finally these gaseous molecules may be allowed to come together to form the crystal (with liberation of the heat of sublimation S_{NaCl}). In both cases the end product is one gramme-molecule of crystalline NaCl.

The direct heat of formation B from the elements (see above) may therefore be expressed by the equations:

$$B = -(S_{\mathrm{Na}} + \tfrac{1}{2}D_{\mathrm{Cl}_2} + I_{\mathrm{Na}}) + E_{\mathrm{Cl}} + L_{\mathrm{NaCl}}$$

---

* Square brackets denote the solid state and round brackets the gaseous state.

or $$B = -(S_{Na} + \tfrac{1}{2}D_{Cl_2} + I_{Na}) + E_{Cl} + V_{NaCl} + S_{NaCl}.$$

By means of the first of these equations the lattice energy L can be calculated from observable quantities and the result compared with the theoretical value. The agreement obtained is good.

The theory also enables us to calculate a number of other physical properties. For instance, a detailed calculation shows that in all binary salts (i.e. salts with two ions) the compressibility depends only upon the interionic distance. This deduction is confirmed by experiment. The actual values of the compressibility give the index *m* which occurs in the repulsion term (see p. 409). This is nearly always approximately 10.

There are, however, a great many properties which cannot be accounted for satisfactorily by the theory. Thus from the law of force between the ions it is possible to calculate the breaking stress of a salt (Vol. I, p. 210). The value obtained for NaCl is 2×10^{10} dynes/cm.^{2}. Experiment, however, gives a value nearly 1/400 of this, namely $5{\cdot}3 \times 10^7$ dynes/cm.^{2}. If the determination is carried out under water, the result observed is considerably nearer the theoretical value. The remarkably low value obtained in air must therefore be due in part to imperfections and tiny cracks in the surface of the crystal under investigation.

This example shows that the theory explained above is not capable of accounting for all properties of *real* crystals. As has been pointed out by SMEKAL in particular, the reason for this seems to be that the perfectly regular lattice arrangement assumed in the theory is only realized, even in the most perfect crystals, over small regions containing about 10^5 to 10^6 molecules. The large single crystal is made up of many such regions placed together with mutual displacements and probably also different orientations (*mosaic structure*). Between the elements of the mosaic there are crystal imperfections * at which the forces holding the crystal together are impaired. These imperfections appear to play an essential part in many phenomena (e.g. the effects of small traces of impurities, which may take up positions at the imperfections, on electrical conductivity, mechanical properties, phosphorescence, photo-electric conductivity, diffusion phenomena, &c.).

There is also a discrepancy between the observed and the theoretically-calculated dielectric strengths (Vol. III, p. 660) of crystals. The break-down field strength observed experimentally for NaCl is about 2×10^5 volts/cm., whereas the value to be expected from the lattice theory is $1{\cdot}5 \times 10^8$ volts/cm. This is the calculated field strength required to pull the ions apart from their combination in the lattice, and so to initiate an electric discharge. JOFFÉ appears to have attained the theoretical dielectric strength with very thin crystal layers, e.g.

* Ger. *Lockerstellen.*

mica plates. The reason for the discrepancy between theory and experiment lies partly in the fact that the ions in the crystal perform thermal motions, as a result of which the lattice linkages are not so strong as is assumed in the theory. To improve the agreement, the measurements of dielectric strength must be made at sufficiently low temperatures, for which the thermal motions are small. Moreover, the applied electric field sets free those ions which are at imperfections in the crystal and thus are less strongly held than the rest. These ions may then be accelerated by the field and may liberate other ions from the lattice by collision. In this way a discharge may be set up and break-down of the crystal may ensue. In very thin crystal layers the length of path of a moving ion is very small and so also is the number of ions which it can liberate by collision. Hence there is no possibility of a break-down being started in this way (compare Vol. III, p. 339); only a small current can be detected. For glass and mica it is found that the dielectric strength, which for layers of ordinary thickness is about 3×10^5 volts/cm., gradually rises as the thickness is diminished to 2×10^{-5} cm., until it almost attains the theoretical value. Further decrease of thickness then produces no further change in the dielectric strength.

3. Vibrations in Solid Bodies

In consequence of their thermal energy, the individual lattice points of a crystal execute vibrations relative to one another. The lattice energy L (the lattice points being assumed at rest) is thereby increased by the thermal energy U, given by the equation

$$U = \int_0^T C_v dT.$$

The specific heat C_v at constant volume is not a constant, but falls off rapidly at low temperatures (see Vol. II, p. 44).

The Specific Heat of Solids.—The approximate validity of the rule of DULONG and PETIT (Vol II, p. 24) at medium temperatures shows that we may expect similar behaviour from all simple solids, i.e. solids which are built up of similar atoms, so that all the lattice points may be regarded as being equivalent. The value of the constant in the rule of DULONG and PETIT, namely $C_v = 6$ cal. per gramme-atom, indicates a distribution over six degrees of freedom (Vol. II, p. 41). The atoms in the lattice can perform oscillations in all directions about their positions of equilibrium. Now three-dimensional oscillators of this kind (assumed harmonic) do indeed possess six degrees of freedom, three for kinetic energy and three for potential energy.

The marked decrease in the specific heat at low temperatures means that the number of degrees of freedom must be decreased; certain vibrations must cease. The reason for this lies in the quantization of the behaviour of the atoms. As has been shown on p. 264, the possible energy states of a linear oscillator are given by the equation $E = (n + \frac{1}{2})h\nu$, where n is an integer. Transference of vibrational energy from one atom to another therefore cannot occur in amounts less than $h\nu$.

Now thermal energy is distributed amongst the atoms. Continuous (non-quantized) distribution is governed by the MAXWELL-BOLTZMANN law (Vol. II, p. 47) which in the case of two degrees of freedom gives the result that the number N_E of molecules with energies exceeding E is

$$N_E = Ne^{-E/kT},$$

where N is the total number of molecules considered. An oscillating atom, considered as a *linear* oscillator with one frequency, possesses two degrees of freedom. The above result remains true for such an oscillator even when the energy distribution is no longer continuous (as for kinetic energy of translation) but quantized (as for vibrational energy). The sole difference is that in the latter case only certain definite energies, given by $E = (n + \frac{1}{2})h\nu$, are permissible. We may ignore the zero-point energy $\frac{1}{2}h\nu$, as it contributes nothing to the specific heat. We are then left with the possible energies $E = h\nu$, $2h\nu$, $3h\nu$, &c. According to the law of distribution, the numbers of atoms possessing energies greater than $nh\nu$ and $(n + 1)h\nu$ are respectively

$$Ne^{-nh\nu/kT} \quad \text{and} \quad Ne^{-(n+1)h\nu/kT}.$$

By subtraction, therefore, the number N_n of atoms possessing exactly the energy $nh\nu$ is

$$N_n = Ne^{-nh\nu/kT}(1 - e^{-h\nu/kT}) = KNe^{-nh\nu/kT},$$

where $K = 1 - e^{-h\nu/kT}$ is a constant at a given temperature. Thus the number of atoms possessing one vibrational quantum is $N_1 = KNe^{-h\nu/kT}$; the number possessing two vibrational quanta is $N_2 = KNe^{-2h\nu/kT}$, and so on. The total energy of all the vibrating atoms is obviously given by

$$\begin{aligned} U &= h\nu(N_1 + 2N_2 + 3N_3 + \ldots) \\ &= KNh\nu(e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} + \ldots). \end{aligned}$$

Remembering that

$$\frac{x}{(1 - x)^2} = x + 2x^2 + 3x^3 + \ldots,$$

we see that

$$U = KNh\nu \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2}.$$

Substituting the value of K as given above, we obtain

$$U = Nh\nu \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \frac{Nh\nu}{e^{h\nu/kT} - 1}.$$

If we consider a gramme-molecule, we have $Nk = R$ (see Vol. II, pp. 39 and 41). We may also introduce the quantity $\theta = h\nu/k = 4{\cdot}78 \times 10^{-11}\nu$. We thus obtain

$$U = \frac{R\theta}{e^{\theta/T} - 1}.$$

The specific heat C_v per gramme-molecule is obtained by differentiating with respect to T, which gives

$$C_v = \frac{dU}{dT} = \frac{R(\theta/T)^2 e^{\theta/T}}{(e^{\theta/T} - 1)^2}.$$

This value of C_v must be multiplied by 3 on account of the fact that the oscillators are not linear (2 degrees of freedom) as assumed above, but spatial (6 degrees of freedom). It is then in good agreement with experiment, as far as simple solids (p. 402) are concerned (compare Vol. II, p. 44).

The quantity θ has the dimensions of a temperature, and is called the *characteristic temperature*. It is directly proportional to ν for any substance and represents the temperature at which $h\nu = kT$ in accordance with classical theory.

By means of the above equation it is possible to deduce θ from the experimentally-observed variation of C_v with T. Hence the percentage of the atoms possessing n vibrational quanta at any given temperature can be calculated. Thus diamond has the very high value $\theta = 1295$ and the distribution of vibrational energy amongst the atoms at T = 130° abs. is 99·995 per cent with $n = 0$ and 0·004 per cent with $n = 1$. Thus even at this relatively high temperature the thermal energy of vibration is practically non-existent. Even as high as T = 386° abs. (i.e. + 113° C.) the distribution is: 95 per cent with $n = 0$, 4·75 per cent with $n = 1$, 0·23 per cent with $n = 2$, and only 0·01 per cent with $n = 3$. For lead, which has $\theta = 67$, the distribution at T = 67° abs. is the same as that for diamond at 1295° abs., namely, 63·3 per cent with $n = 1$, 23·3 per cent with $n = 2$, 8·6 per cent with $n = 3$, 3·1 per cent with $n = 4$, 1·2 per cent with $n = 5$.

The formulæ obtained above are in good general agreement with experimental observations. At very low temperatures, however, discrepancies arise, since in this region the specific heat increases proportionally to T^3. In 1912 Debye * was able to show that this was due to the too great simplicity of the assumption of only *one* frequency for the oscillators (see above). In the complete treatment it is necessary to assume a large number of frequencies, which are regarded as elastic waves passing through the solid, being reflected at its boundaries and thus giving rise to stationary waves. Not all wave-lengths can form these stationary waves, only those which give an exact number of half wave-lengths. It is easy to see that the smaller the wave-length, the closer together do the possible wave-lengths lie. There is, however, a certain minimum wave-length below which no more are possible; for the waves are propagated by the atoms, so that the wave-lengths must be at least of the order of magnitude of the interatomic distances. The distribution of possible frequencies is therefore of the type shown in fig. 10. From this we see that (at least for simple solids) the greatest concentration of frequencies is near the upper limit (i.e. the lower limit of wave-length). This explains the approximate validity of the theory in which only one frequency is assumed. At very low temperatures, however, where the high frequencies die out on account of their large $h\nu$-values, the existence of the slower vibrations becomes important.

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* P. Debye, Dutch by birth (born 1884), was first Professor of Physics at Göttingen, then (1920–7) at the Technical College at Zürich, and subsequently at Leipzig.

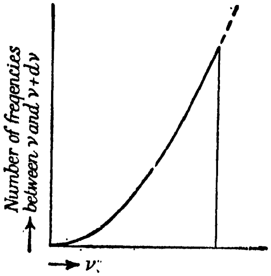

Fig. 10.—Distribution of frequencies of thermal vibration in a solid (after Debye).

Optical Vibrations in Crystals.—Since the vibrating particles in ionic lattices are electrically charged, their proper vibrations can give resonance effects with electromagnetic waves. Light of frequencies equal to proper frequencies of the crystal is very strongly absorbed, the selective absorption being accompanied by metallic reflection. Hence these proper frequencies can be determined by measuring the absorbing and reflecting powers of the ionic crystal. The frequencies are always found to lie in the infra-red region. Two groups may be distinguished: one in the long-wave infra-red in the wave-length range 23μ to 152μ and the other in the short-wave infra-red between 10μ and 20μ.

The method of investigation consists in splitting up the infra-red rays from a source into a spectrum, and then measuring the coefficient of absorption or reflection of the crystal at successive wave-lengths. Fig. 11 is a diagram showing how the apparatus is arranged. The radiation from a continuous source L is focussed on the slit S_1 of a grating monochromator by means of the concave mirror H_1. The monochromator consists of the slits S_1 and S_2, the grating G, and the concave mirrors H_2 and H_3. The narrow wave-length region passing out through the slit S_2 is directed on to the crystal K by the mirror H_4. The beam reflected from the crystal is then focussed by the mirror H_5 on to the thermopile T, where it produces an electric current which is measured by a galvanometer. The galvanometer deflection is a measure of the intensity of reflection from the crystal. By adjusting the setting of the monochromator the wave-length of the radiation falling upon the crystal can be varied at will. In these infra-red investigations concave mirrors are used instead of lenses because of their freedom from chromatic aberration. Infra-red radiation is detected and measured by thermoelectric methods, as the sensitivity of photographic plates only extends to about 1·5μ.

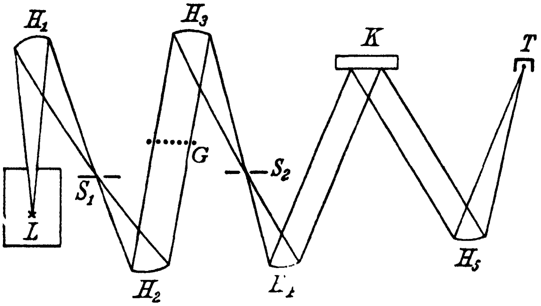

Fig. 11.—Diagram showing arrangement of apparatus for infra-red investigations

Spectrometric measurements can be carried out up to wave-lengths of about 30μ. To investigate waves of greater length, we make use of the method of so-called **residual rays***, which depends on the fact that light of the proper frequency of the crystal is reflected very strongly. The radiation from a continuous source is reflected a number of times from the crystalline substance under investigation, until after the last reflection practically nothing is left but the proper frequency, all the others having been largely absorbed. The light remaining after the series of reflections is referred to as *residual rays*. The wave-lengths in the long-wave region are determined by means of a Fabry-Pérot interferometer (Vol. IV, p. 194). The residual rays of long and short wave-length can be separated by means of quartz lenses. The refractive index of quartz for the longer waves ($> 50\mu$) is over 2, and for shorter waves only about 1·5; hence the focal length of a quartz lens is considerably shorter for the longer waves than for the shorter waves. Repeated focussing for the longer waves therefore results in the shorter waves becoming so diffuse as to be negligible.

Fig. 12 shows reflection curves for alkali halides obtained in this way. Wave-lengths are plotted as abscissæ and percentage reflections as ordinates. Increase of ionic mass is seen to be associated with increase of the wave-length of the proper lattice vibration. The residual rays for which this figure is plotted all belong to the long-wave group. The position of the reflection maximum is characteristic of each particular lattice. Examples of the short-wave group are shown in fig. 13, which gives the reflection curves for some carbonates. We see that the reflection maxima of all the carbonates lie at the same positions. The corresponding frequencies are characteristic of all carbonates. In the same way, all salts with polyatomic anions or cations possess their own proper frequencies, e.g. all sulphates have proper vibrations at 9μ and 16μ and all ammonium salts at $3{\cdot}2\mu$, $5{\cdot}9\mu$, and $7{\cdot}0\mu$.

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* The German term *Reststrahlen* is also used in English.

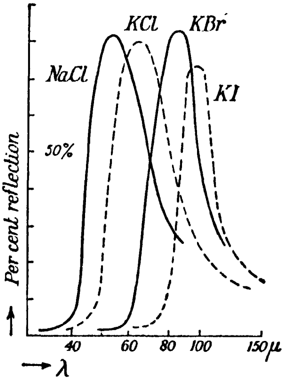

Fig. 12.—Reflection curves of alkali halides in the infra-red (after Liebisch and Rubens).

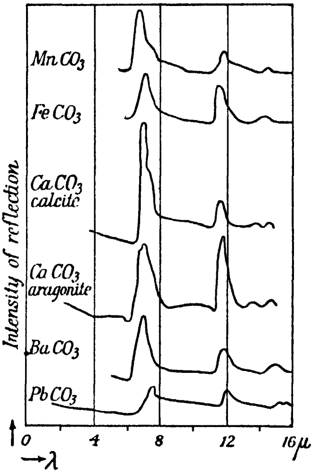

Fig. 13.—Infra-red reflection from carbonates (after Schaefer and Schubert).

The reason for the appearance of these infra-red absorption regions is as follows. The incident electromagnetic waves act on the positively and negatively charged particles in the lattice, causing forced vibrations. The amplitude of these vibrations becomes especially large when resonance occurs (Vol. II, p. 198), i.e. when the frequency of the oscillations of the field of the incident waves is equal to a proper frequency of the charged particles of the crystal. Since the forces linking the charged particles are practically the same throughout the whole crystal, the frequency of vibration of positive relative to negative is fairly sharply defined. The long-wave residual rays correspond to vibrations of the positive and negative ions relative to one another. The frequency increases with increase of the rigidity of the interionic linkages and with decrease of ionic mass. This explains the differing wave-lengths for the different alkali halides in fig. 12. The short-wave group of residual rays, on the other hand, corresponds to vibrations within polyatomic ions (so-called *inner frequencies*), as is indicated by the identity of the frequencies for all salts with a given polyatomic ion. These inner frequencies can also be observed with solutions of the salts—a fact which proves that the polyatomic ions pass over into solution unchanged. The long-wave frequencies, however, cannot be observed in solution. From the magnitudes of the lattice frequencies it is possible to draw conclusions as to the nature of the linkages involved.

Resonance between the incident light and a vibration of the crystal can only occur if the latter is associated with an oscillating electric dipole moment having a component in the direction of the electric vector of the light. If the dipole moment of the crystal vibration is at right angles to the electric vector of the plane-polarized incident light, then no reflection maximum occurs. Vibrations which are not associated with an electric dipole moment are said to be *optically inactive* and cannot be detected by this method at all. In regular crystals the proper vibrations are of equal intensity in all axial directions. In uniaxial (or biaxial) crystals, however, the electric moments occurring in the two (or three) different directions are different. This can be shown by using polarized light. Fig. 14 shows e.g. the proper vibrations of the uniaxial crystal, sodium potassium sulphate, as measured parallel and at right angles to the optic axis. In this case it is possible to differentiate between two quite distinct vibrations, whereas investigations with natural light only give a faint indication of two maxima.

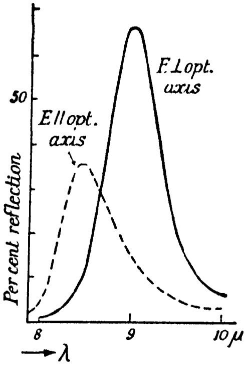

Fig. 14.—Reflection of plane-polarized infra-red radiation by sodium potassium sulphate (after Schaefer and Schubert).

If the lattice points of a crystal are uncharged, the lattice vibrations cannot be detected by means of the absorption of electromagnetic waves. It is possible, however, to detect the elastic waves which pass through the crystal.

Undeformed crystals also have absorption regions in the ultraviolet, due to electronic energy transitions.

Optically *inactive* vibrations can be detected by optical methods when there is coupling with optically *active* oscillations, i.e. with oscillations associated with an oscillating electric dipole moment. This is the case in the scattering of light (Raman spectra, p. 380) and also in the phosphorescence spectra of crystals (TOMASCHEK). If the exciting energy is sufficiently high, the optically active crystal frequencies can, of course also occur in *emission*.

Other Methods for the Determination of Crystal Lattice Frequencies.—The proper vibration frequencies of solids (at least of simple solids, p. 402) can also be deduced by other methods, though in general these do not do more than give the approximate position of the high-frequency limit (see fig. 10, p. 415). The restoring force acting on an atom which is displaced from its equilibrium position is measured approximately by the resistance of the solid to compression. Hence the compressibility χ must be related to the vibrational frequency ν_0. The relation actually obtained is

$$\nu_0 \sim \frac{3 \times 10^7}{A^{\frac{1}{3}} \chi^{\frac{1}{2}} \rho^{\frac{1}{6}}} \text{ sec.}^{-1},$$

where A is the atomic weight and ρ the density. Another form of the relation is

$$\nu_0 = 2{\cdot}91 \times 10^{11} \sqrt{\frac{1}{AV^{\frac{2}{3}}} \left(\frac{C_v}{a}\right)} \text{ sec.}^{-1},$$

in which V is the atomic volume, C_v the atomic heat, and a the coefficient of thermal expansion. Since v, the velocity of sound in the crystal, is also determined by the elastic forces, it too is related to the proper frequency by the equation

$$\nu_0 = \bar{v} \sqrt[3]{\frac{3N}{4\pi V}}.$$

Here $\bar{v}$ is a mean velocity of sound (for longitudinal and transverse waves) and N is Avogadro's number. In Vol. II, p. 44, another formula is given, by means of which a value for ν can be calculated from the melting-point.

Although there are often considerable discrepancies between the ν-values calculated by the different methods, satisfactory agreement is obtained in many cases.

The following is a list of characteristic temperatures θ, as calculated for a few substances by the various methods mentioned above. The representation of the vibrations in a crystal by means of *one* proper frequency (or *one* limiting frequency) is only permissible when the lattice may be regarded as an atomic lattice. In substances of more

TABLE XXXIX

Method	Pb	KCl	Cu	Diamond
Compressibility ..	126	192	327	—
Thermal expansion ..	105	—	325	1860
Velocity of sound ..	75	227	341	—
Melting-point ..	89	271	326	1564
Optical method ..	—	230	—	—
C_v*	88	230	315	1860

* Taking account of the vibrational spectrum.

complicated structure so many proper frequencies occur that it is almost impossible to disentangle them.

4. Liquids

Between the two extreme states of aggregation of matter—perfect gas and crystal—lies the region of real gases and liquids, about which relatively little is known. According to the van der Waals theory, there is a continuous transition between the gaseous state and the liquid state, which can be treated exactly by the equation of state referred to in Vol. II, p. 90. A liquid, then, may be regarded as a highly-compressed gas which is not maintained in its state of compression by pressure applied externally, but by the forces of attraction between its molecules. There are a number of problems, however, which cannot be solved by this theory, particularly problems concerned with the spatial arrangement and motions of the molecules of a liquid. It is found that liquids possess properties similar to those of solids, so that we must assume the presence in liquids of couplings between the individual molecules, similar to those occurring in solids. Thus the motion of any particular molecule in a liquid depends on the motions of the neighbouring molecules.

The Scattering of Light by Liquids.—The thermal motions of the molecules of a solid may be regarded as a superposition of elastic waves (fig. 10, p. 415). An incident light beam will be scattered by these waves. As is indicated in fig. 15, the scattering may be thought of as due to reflection at the wave-fronts, just as in the Bragg theory of the reflection of X-rays at the lattice planes of a crystal (p. 68). Thus for given directions of incidence and observation only waves with fronts equally inclined to these two directions will be effective, and among such waves, only those with a particular wave-length. Different directions of observation will correspond to different suitably oriented waves. Then the wave-fronts of the elastic waves constitute moving reflectors for the light, so that a Doppler effect must arise. Hence we may anticipate that incident monochromatic light will be split up into two distinct frequencies by reflection at the moving elastic waves. Instead of the original frequency ν we may expect to get two frequencies $\nu \pm \Delta\nu$, where $\Delta\nu = v/\lambda$, v being the velocity of the elastic waves (i.e. the velocity of sound) and λ the wave-length of the elastic waves in the liquid. An experiment of the kind outlined here will therefore throw light on the question whether the molecules of the liquid move

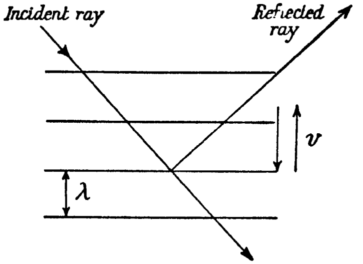

Fig. 15.—Reflection of light by acoustic waves

freely and independently, like those of a gas, or whether there is a strong coupling between them, as in a solid. With the first of these alternatives the scattering of light would result in a broadening of the incident frequency, owing to the Doppler effects of the random motions of the scattering molecules. With the second alternative, on the other hand, we should expect a distinct splitting into the two components mentioned above.

Investigations carried out in Debye's laboratory (using the mercury line 4358 Å. and the zinc line 4680 Å.) have actually demonstrated the occurrence of lines of modified frequency in the scattering of monochromatic light by liquids. It was found, however, that a line of unmodified frequency is also present in the scattered spectrum, although, according to the calculations of Brillouin, such a line is not to be expected. Thus these experiments prove that there must be a strong coupling between each molecule and its neighbours in liquids, as a result of which the molecules can probably perform a kind of vibration. The vibrations of a given molecule do not, however, take place about a fixed point in the substance (as is the case in solids); but rather about a point whose position moves about relatively slowly in the liquid. This view is also in agreement with the atomic heats of monatomic liquids, e.g. mercury with $C_v = 5{\cdot}87$ cal. per gramme-atom, which correspond to the Dulong and Petit value for solids and indicate the existence of six degrees of freedom.

Debye and Sears have also succeeded in demonstrating the reflection of light at artificially-produced acoustic waves. With the help of an oscillating quartz crystal of high frequency they excited supersonic waves (with a wave-length of a few tenths of a millimetre) in a liquid, and then found that a beam of light is diffracted by the liquid in just the same way as by an optical grating. This may be explained by assuming that the acoustic waves produce a regular succession of condensations and rarefactions throughout the liquid, and that these act as the lines and spaces of a grating. The phenomenon provides a convenient method for determining the velocity of sound in a liquid, and hence its compressibility (see fig. 16).

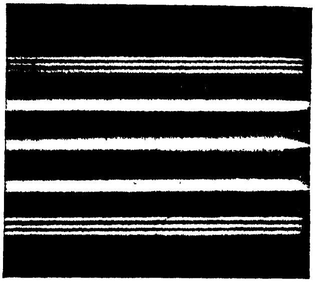

Fig. 16.—Grating spectra of various orders produced by very short acoustic waves in water (after Lucas and Biquard).

The Scattering of X-rays by Liquids.—Observation of the X-ray diffraction effects of liquids may be expected to give information about regularities in the arrangement of the molecules, the distances between which are of the same order of magnitude as the wave-lengths of X-rays. Actual experiments do in fact give such effects, but compared with the effects obtained with crystals they are rather vague. Yet the results prove that regularities of arrangement must be present, and that the distances involved are of the expected order of magnitude

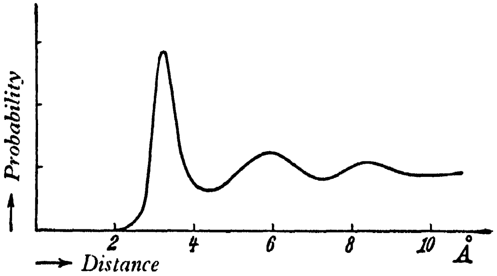

Fig. 17.—Probability of occurrence of various interatomic distances in liquid mercury, as deduced from X-ray diffraction (after Debye)

(see fig. 17). So far it is not possible to give precise information about the arrangements of molecules in liquids; but we may assume that there must be a lattice-like structure extending at least over small regions, although the individual lattice points must be continually changing places.

The diffraction effects just referred to must be distinguished from other superimposed diffraction effects due to the regular arrangement of the atoms within the individual molecules, which also involves distances of about the same magnitude. These latter effects are those which are observed for vapours. In addition to liquids, therefore, Debye has investigated vapours. He finds marked diffraction effects in the vapours of substances with polyatomic molecules (e.g. CCl_4, see p. 251), whereas in monatomic vapours (e.g. Hg) scattering is alone observed.

CHAPTER VIII

Electrodynamics of Moving Media

1. The Effect of Motion on Optical Phenomena

The Problem of "Absolute Motion".—Phenomena involving the effect of the motion of material bodies on electromagnetic processes are of great importance in fundamental physical theory, for they are most intimately concerned with the problem of the interaction between matter and ether. The experiments of this type which have been performed are especially interesting in that they have revealed a behaviour essentially different from that anticipated from tentative theoretical ideas based on other observations. In these tentative theories it was assumed that all space is filled with a substance known as the *ether*, and that the effects produced by the motion of matter are due to movement relative to this ether, which is itself supposed to be at rest. The usual measurements of the velocity of a body merely give the velocity relative to some other arbitrarily chosen body; but according to the views just mentioned it must also be possible, by means of experiments on the effect of motion upon electromagnetic phenomena, to determine the *absolute* velocity of a body, i.e. its velocity relative to the ether which fills all space and is the carrier of electromagnetic phenomena. It is found, however, that the problem of "absolute" motion is by no means so simple as this, and the interpretation of the various experimentally-observed facts has formed one of the most burning questions in physics for more than a century. We shall first give an account of the experimental data.

The nature of the problem will be clear from the following example. Imagine two bodies A and B moving in any manner whatever. The motion of B may be described by regarding A as at rest and stating the velocity of B relative to A. Conversely, the body B may be assumed as at rest and the motion of A described as relative to it. The question at once arises (and this is the fundamental problem in its simplest form), which of the two bodies is really in motion? According to the views referred to above, it must be the one which is moving relative to the ether, i.e. the one for which modifications of electromagnetic phenomena are observable. Is it in fact possible to determine absolute motions in this way, and what are the modifications of electromagnetic phenomena involved? Or has the idea of absolute motion no physical meaning, and must we speak only of motion relative to material systems of reference?

Effect of the Motion of the Source on the Velocity of Light.—From the experimental evidence hitherto accumulated it must be concluded that *the velocity of propagation of light is independent of the motion of the source from which it is emitted.*

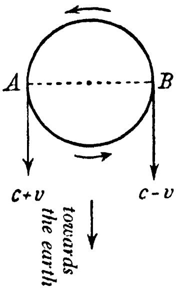

Fig. 1.—Velocity of light from a double star.

This follows from observations upon double stars (so-called *binaries*) in the direction of motion. The motions of double stars, as observed directly or spectroscopically (i.e. by the Doppler displacements of spectral lines) can be satisfactorily explained by Kepler's laws on the assumption that the velocity of light is unaffected by the motions. Consider the case of a binary system (fig. 1) whose orbital plane contains the direction of observation of a terrestrial observer. If the velocity of light *relative to the star* were c, then the velocity of light relative to the observer (assumed at rest) would be $c+v$ at the point A and $c-v$ at the point B. Owing to the greater rate of advance of the light from A, the arrival of the star at A would be observed too early as compared with its arrival at B. In certain circumstances the two times of arrival might even appear to be simultaneous. Actually the times at which the star is at A and B can be determined from the maxima of the Doppler effect. Observations upon a suitable system (*β Aurigae*) have proved that the variation of the velocity of light throughout the whole orbit must certainly be less than $2{\cdot}5 \times 10^{-7}$ of the velocity of the star.

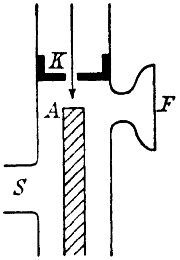

Fig. 2.—Stark's experiment on the velocity of propagation of light emitted by atoms in motion and atoms at rest:

K, cathode; A, anode; F, window; S, connexion to pump.

Observations at right angles to the direction of motion have been made by J. Stark on positive rays of hydrogen. The positively-charged hydrogen atoms fly through the hole in the cathode K (fig. 2) with velocities up to 10^8 cm. per second, and strike against the metal surface A. The space also contains mercury vapour at rest. Emission of light from the moving hydrogen atoms and the mercury atoms at rest can be observed immediately in front of A. An image of this emitting region is focussed on the slit of a spectrograph placed outside the window F. The observation is thus at right angles to the direction of motion of the hydrogen atoms, the spectrograph slit being parallel to this direction. In these circumstances the length of the spectral lines obtained will be limited by the metal surface A. If now the motion of the hydrogen atoms imparts a lateral velocity component to the light emitted from them, there must be a lengthening of the hydrogen lines as compared with the lines emitted by the mercury atoms at rest. For the actual experiment the calculated elongation was about 1·2 mm., but no trace of it could be observed. Thus the velocity of the light emitted from the hydrogen atoms must be the same as that of the light emitted by the mercury atoms. The propagation of light is unaffected by the motion of the source.

Doppler Effect.—The effect of the motion of the source on the frequency of the light as determined by an observer has been discussed on p. 219. The frequency is altered in accordance with the equation

$$\nu' = \nu\left(1 \pm \frac{v_r}{c}\right),$$

where v_r is the velocity of the source relative to the observer. This equation has been thoroughly confirmed by observations upon terrestrial and celestial sources.

Aberration.—In 1725 Bradley * observed small periodic changes in the apparent position of the star γ *Draconis*. More detailed investigation has shown that all the fixed stars exhibit these changes of apparent position, which are due entirely to the motion of the earth round the sun. The phenomenon is called *aberration*. Every star appears to describe an ellipse with a period of one year and a semimajor axis which lies parallel to the ecliptic (the plane of the earth's orbit) and subtends an angle $\alpha = 20{\cdot}47''$. For stars situated in the ecliptic the motion is on a straight line (ellipse of zero minor axis): for stars at the pole of the ecliptic the motion is circular. The apparent displacement of the stars is always *in the direction* of the earth's orbital motion.

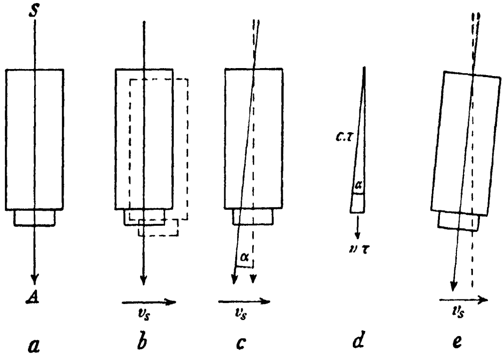

Fig. 3.—Diagram to explain aberration

The explanation of aberration is as follows. Consider a ray of light SA (fig. 3*a*) passing through a telescope at rest, as shown in the figure. Now let the telescope be moving with the velocity v_s at right angles to the direction of the ray. A light quantum, which enters the telescope through the middle of the objective, passes through the instrument with velocity c, while at the same time the telescope moves laterally with velocity v_s. If τ is the time which the light takes to traverse the length of the telescope, the distance through which the telescope moves during this time is $v_s\tau$, the new position being shown diagrammatically by the dotted lines in fig. 3*b*. It is clear that the light quantum will not leave the telescope through the middle of the eye-piece (as it did when the telescope was at rest, fig. 3*a*), but somewhat to the side. Relative to the telescope, therefore, we obtain the figure shown in fig. 3*c*, the angle α between the ray and the axis of the telescope (see fig. 3*d*) being given * by

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* James Bradley (1693–1762), Astronomer Royal from 1742 to 1752.

$$\sin\alpha = \frac{v_s\tau}{c\tau} = \frac{v_s}{c}.$$

The telescope must therefore be inclined at this angle in order to bring the image of the source of light (i.e. the star in question) into the middle of the field of view. As can be seen from fig. 3*e*, the telescope must be tilted *forwards* in the direction of its motion.

The apparent displacements of the positions of the fixed stars can therefore be calculated from v_s, the component of the earth's velocity at right angles to the direction of observation. The mean velocity of the earth in its orbit is 30 km. per second (i.e. 3×10^6 cm. per second), whence we obtain $\alpha = v_s/c = 3 \times 10^6/(3 \times 10^{10}) = 10^{-4}$ radian $= 20{\cdot}6''$. More accurate data give $\alpha = 20{\cdot}47''$, the uncertainty lying mainly in the value of the mean orbital velocity of the earth.

It is important that the student should clearly realize that this aberration is only observable because of the non-uniformity of the earth's motion. If the motion of the earth were uniform and rectilinear, all the stars would be subject to the same apparent displacement relative to the positions which they would appear to occupy if the earth were at rest. This displacement could never be determined, however, because the position corresponding to the earth at rest would be unknown. The observed displacements are due to the non-uniformity of v_s. Thus aberration belongs to a class of phenomena characteristic of non-uniform motion, e.g. the **Foucault** pendulum experiment.

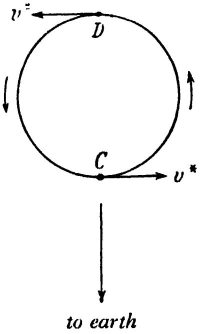

Fig. 4.—Aberration of a double star

Aberration is accordingly *independent* of the motions of the stars and consequently *not dependent* on the relative motion of the stars with respect to the earth. This is confirmed by observations on double stars. As **Lenard** has shown, these exhibit normal aberration. If the aberration were dependent on the relative motion, binary systems would show a marked apparent lateral separation of the positions C and D of fig. 4. Actually no such separation is observed.

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* Here it is assumed that the velocity of light is c relative to the system of reference in which the telescope is at rest (see p. 444). This makes only a negligible second-order difference as compared with the assumption that the velocity of light is c relative to the system of reference used in measuring $\mathbf{v}$.

"Ether Drag".—When light is passed through a material medium (e.g. flowing water) which is moving with a velocity v relative to an observer, the velocity of light (i.e. the *phase velocity*) as measured by this observer is given by the equation

$$V = \frac{c}{\mu} \pm \left(1 - \frac{1}{\mu^2}\right)v = c\left[\frac{1}{\mu} \pm \left(1 - \frac{1}{\mu^2}\right)\frac{v}{c}\right],$$

in which μ is the refractive index of the medium. The quantity

$$1 - \frac{1}{\mu^2} = \epsilon$$

is called Fresnel's *coefficient of ether drag* (FRESNEL, 1818).

The following point must be borne in mind in connexion with the refractive index μ. Owing to the motion of the medium, the frequency of the light relative to the medium as compared with the frequency observed by the observer is modified by the Doppler effect. The refractive index in the formula must be that for the frequency relative to the medium.

The first experimental determination was made by FIZEAU in 1851. Further experiments were carried out by MICHELSON and MORLEY (1886) and very accurate measurements were made by ZEEMAN (1914). The principle of the experimental apparatus is illustrated in fig. 5.

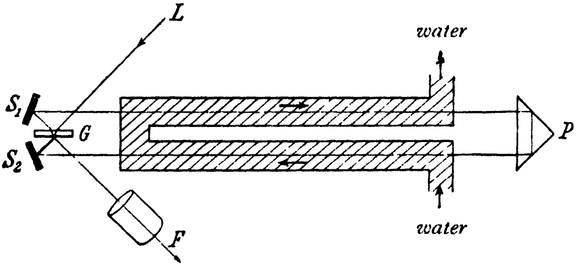

Fig. 5.—Diagram of apparatus for measuring the ether drag in moving water

Light from a source L is incident on a half-silvered plate G, by means of which it is divided up into two partial beams. One is reflected to the mirror S_1 and thence to the prism P, where it is twice reflected and passes to the mirror S_2 and thence back to the plate G. The other partial beam traverses just the opposite path. The two beams are united again at the plate G, and the interference phenomena due to their superposition are observed in the telescope F (as in the Michelson interferometer, Vol. IV, p. 190). On the way between the mirrors S_1 and S_2 and the prism P the beams pass through tubes (in ZEEMAN's experiments these were about 3 metres long) in which water is flowing (at a speed of about 5 metres per second). The direction of the flow of the water is arranged (see fig. 5) so as to be the same as that of one of the partial beams and opposite to that of the other. Thus if the moving medium drags along the ether with it, the effect will be to accelerate one partial beam and retard the other. This will mean an optical path difference and a consequent displacement of the interference fringes from their positions when the water is at rest. The displacements observed in the actual experiments were of the order of $\frac{1}{2}$ to 1 fringe-breadth. It was found that the observations were in good agreement with the Fresnel formula given above (account being taken of the proper value of μ to be used—see above). The refractive index of water being about 4/3, we have $\epsilon = 7/16$, i.e. approximately $\frac{1}{2}$. Thus the velocity of propagation of the phase of the light waves is altered by about half the velocity of flow of the water. ZEEMAN has also carried out experiments with moving solid bodies (cylinders of glass and quartz). Good agreement was again obtained between observation and the formula.

It is important that the student should clearly realize that the phenomena are *not* due to a partial carrying along of the ether by the moving medium, such as is suggested by the term "coefficient of ether drag". The name "ether drag" is a relic from earlier times. What is actually observed is an alteration of *phase* velocity, i.e. in a certain sense a change of the refractive index of the medium (distinct from that due to the Doppler effect). The velocity of light relative to the observer being c, a greater number of molecules will be encountered by the light per second when the medium is moving against the light than when the medium is at rest. Now the diminution of *phase* velocity in the medium (corresponding to the refractive index) is due to the superposition of the elementary waves scattered from the individual molecules of the medium. Motion of the medium against the direction of propagation of the light must therefore have the same effect as if the medium became denser (the properties of the molecules otherwise remaining unaltered), i.e. must result in an increase of refractive index and a corresponding diminution of the phase velocity of the light. In 1895 H. A. LORENTZ proved from the electron theory of dispersion that this diminution must be in accordance with the Fresnel formula. There is, however, no reason to doubt that even in a medium moving in a terrestrial laboratory the *signal velocity* (Vol. IV, p. 172) is c relative to an observer who is at rest in the medium. In the propagation of light through a material medium the wave-head does not keep the same phase (as it does e.g. in a vacuum, where the phase velocity is equal to the signal velocity), but is continually varying in phase in such a way that it glides forward (as it were) over the more slowly advancing phase motion.

The fact that masses of matter such as are available for investigation in the laboratory do *not* drag along the ether to an appreciable extent has been demonstrated by LODGE.* He used an interferometric apparatus similar in principle to that shown in fig. 5, and investigated light which had passed very close to large rotating discs of steel. No effect upon the velocity of the light could be detected, even when the discs were strongly electrified or magnetized. Any dragging along of the ether which may occur is so small that the consequent alteration of the velocity of light is certainly less than 1/1000 of the velocity of rotation.

The Part played by Ether Drag in Experiments on the Effect of Motion on Electromagnetic Phenomena.—The value of the coefficient of ether drag occurring in the Fresnel formula is of great importance in so far as it indicates that the optical result of an experiment on the effect of motion must remain unaffected by the interposition of a material medium (except for effects of the second order, i.e. proportional to $(v/c)^2$). Some examples of this will now be considered in more detail.

We shall find it convenient to adopt the following nomenclature. The direction of the wave-normals, i.e. the direction of advance of the wave motion relative to the system at rest, will be called the *absolute ray*. On the other hand, the path of the light relative to the moving medium will be called the *relative ray*. The meaning of these terms will be clear from fig. 3, *c* and *e* (p. 425), in which the dotted line is the absolute ray and the corresponding continuous line the relative ray. As a result of ether drag, *all optical laws of media at rest remain valid to a first approximation* † *for the relative rays in moving media.*

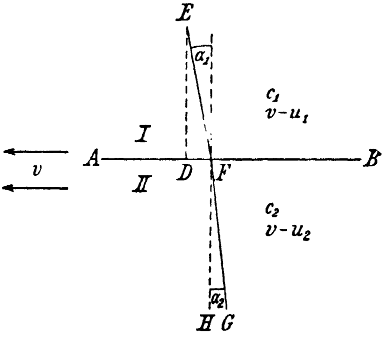

Fig. 6.—Validity of the law of refraction for relative rays

As an example we may choose the *law of refraction*. Let AB in fig. 6 be the surface of separation of two media I and II. Let the wave-fronts of the incident light waves be parallel to AB, i.e. let the absolute ray ED be normal to the interface. Further, suppose that the velocity of propagation in the medium I is c_1

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* Sir OLIVER LODGE (1851–1940) was Professor of Physics at University College, Liverpool, from 1881 to 1900, and then Principal of Birmingham University until 1919. He was also distinguished for his work on lightning, electrolysis, the electron, wireless communication, &c., and was keenly interested in psychical research.

† I.e. neglecting all terms in $(v/c)^2$ and higher powers.

and in the medium II c_2, and that the media are moving with the common velocity v from B towards A. The phase velocity of the light in the direction BA is then less than v in both media. Let it be $v - u_1$ and $v - u_2$ respectively. Light starting from E proceeds to D, relative to a system of reference at rest. On account of the motion of the medium, the path of the light relative to the medium (relative ray) is EF. While the light has travelled from E to D it has drifted relative to the medium, which has thus advanced the distance FD relative to it. We therefore have $\tan \alpha_1 = u_1/c_1$. At the point F the light enters the medium II. The absolute ray remains normal to the interface AB, since normal rays are not refracted. Hence if the second medium were at rest the light would arrive at H. Owing, however, to the motion of the medium and the ether drag, the relative ray is FG, and we have $\tan \alpha_2 = u_2/c_2$. Hence neglecting quantities of the second order of smallness, as is permissible on account of the smallness of the angles, we may write

$$\frac{\sin \alpha_1}{\sin \alpha_2} = \frac{\tan \alpha_1}{\tan \alpha_2} = \frac{u_1 c_2}{u_2 c_1}.$$

Now the ordinary equation for the law of refraction is

$$\frac{\sin \alpha_1}{\sin \alpha_2} = \frac{c_1}{c_2}.$$

If the two equations are to be identical, i.e. if the law of refraction is to remain valid for the moving media, we must have

$$\frac{c_1}{c_2} = \frac{u_1 c_2}{u_2 c_1} \quad \text{or} \quad \frac{u_1}{u_2} = \frac{c_1^2}{c_2^2}.$$

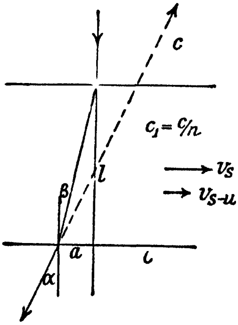

Fig. 7.—Aberration in the case of a telescope filled with water.

In the case in which medium II is a vacuum, $u_2 = v$ and $c_2 = c$, and the condition becomes

$$\frac{u_1}{v} = \frac{c_1^2}{c^2} \quad \text{or} \quad u_1 = \frac{c_1^2}{c^2} v.$$

This means that the velocity imparted to the phase motion of the light by the drag of the movement of the medium I must be

$$v - u_1 = v - \frac{c_1^2}{c^2} = v\left(1 - \frac{1}{\mu^2}\right).$$

But this is exactly the result given by Fresnel's equation (p. 427).

It follows that all experiments on the positions of the fixed stars must give the same results as if the earth were at rest and the stars were displaced through the definite angle of aberration. Thus we can explain the result of the experiment of Airy (1871), who determined the aberration by using a telescope filled with water. Since the velocity of propagation of light in water is less than in air, the water-filled telescope must move through a greater lateral distance than the air-filled telescope during the time of passage of a light quantum through it (compare fig. 3, p. 425). It might therefore be expected that the angle of aberration would be increased by filling the telescope with water. The experiment of Airy, however, showed that the angle of aberration is unaffected. The reason for this negative result is that the light is dragged sideways by an amount which exactly compensates for the slower velocity in the direction of the axis of the telescope. If the lateral velocity of the telescope is v_s, the corresponding lateral velocity of the light (see fig. 7) will be

$$v_s - u = v_s\left(1 - \frac{1}{\mu^2}\right).$$

We have

$$\tan\beta = \frac{u}{c_1} = \frac{a}{l} \sim \sin\beta,$$

and hence, since $\sin\alpha/\sin\beta = \mu$ by the law of refraction, we obtain

$$\sin\alpha = \mu\sin\beta = \frac{\mu u}{c_1} = \frac{\mu}{c_1}\frac{v_s}{\mu^2} = \frac{v_s}{\mu c_1} = \frac{v_s}{c}.$$

This result is independent of μ and the aberration therefore remains the same, no matter what the medium within the telescope is.

Veltmann's Theorem.—It was first shown by VELTMANN (1873), and later more fully by H. A. LORENTZ, that as a result of ether drag a common uniform motion of light source, material medium, and observer cannot have any first-order effect upon optical phenomena. Since in all practicable experiments the light must pass from one station to another and back again, we are always concerned with a closed optical path, such as is represented diagrammatically in fig. 8. When the system is at rest, the time t taken for the propagation of the light from A back again to A is given by

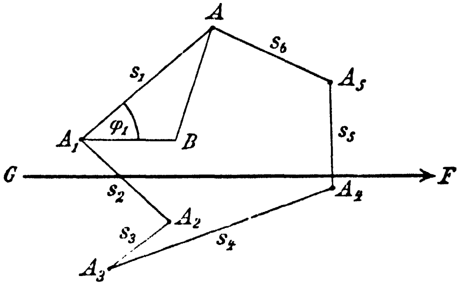

Fig. 8.—Diagram to illustrate Veltmann's theorem

$$t = \sum_1^n \frac{s_n}{c_n} = \frac{s_1}{c_1} + \frac{s_2}{c_2} + \dots .$$

Now let the whole system be moving with the velocity v in the direction from G towards F. Using the notation introduced above, the velocity component imparted to the light by this motion is always

$$v - u_n = v\left(1 - \frac{1}{\mu_n^2}\right),$$

so that in consequence of the motion of the system the light gets a velocity u_n in the direction from F to G relative to the medium. As the optical path remains unaltered by the motion, the relative rays form the same polygon A—A as before. Consider the side AA_1, and let the velocity of the light relative to the moving medium be c_1'. If the time taken by the light to pass from A to A_1 is t_1, we have (see fig. 8)

$$AA_1 = c_1't_1; \quad A_1B = u_1t_1; \quad AB = c_1t_1.$$

Since u_1 is very small, it follows that

$$c_1' = c_1 + u_1 \cos\phi_1,$$

where ϕ_1 is the angle between AA_1 and the direction of motion of the system. Hence

$$t_1 = \frac{s_1}{c_1'} = \frac{s_1}{c_1 + u_1 \cos\phi_1} = \frac{s_1}{c_1} \frac{1}{1 + \frac{u_1}{c_1}\cos\phi_1}.$$

Neglecting quantities involving higher powers of (u_1/c_1) than the first, we have

$$t_1 = \frac{s_1}{c_1'} = \frac{s_1}{c_1}\left(1 - \frac{u_1}{c_1}\cos\phi_1\right) = \frac{s_1}{c_1} - \frac{u_1}{c_1^2} s_1 \cos\phi_1.$$

Corresponding expressions hold for all the other sides of the polygon. The total time t' taken by the light to pass right round the optical path when the system is in motion is therefore

$$t' = \sum_1^n \frac{s_n}{c_n'} = \sum_1^n \frac{s_n}{c_n} - \sum_1^n \frac{u_n}{c_n^2} s_n \cos\phi_n.$$

But for a closed polygon we have

$$\sum_1^n s_n \cos\phi_n = 0.$$

Therefore

$$\sum_1^n \frac{s_n}{c_n'} = \sum_1^n \frac{s_n}{c_n},$$

i.e.

$$t' = t.$$

The Experiments of Sagnac and Harress.—On the other hand, we may expect that the time taken by the light to pass round the polygon will be affected by a *rotational* motion of the whole system; for in this case the light may be moving *with* or *against* the motion of the system throughout the whole of its path. Fig. 9 is a diagram of the experimental arrangement used to investigate this question. Light from the source L is split up at a into two partial beams by means of a half-silvered surface between the two glass plates G_1 and G_2. One of the partial beams is reflected by the mirrors S_1, S_2, S_3, and S_4 in order, and returns to a, while the other traverses the same path in the opposite sense. The two beams then fall superimposed on the photographic plate P, where the interference pattern thus produced is photographed. Let l be the length of an element of the optical path at a distance r from the axis of revolution of the system where the linear velocity of the system is v. The time t_1 which light travelling in the same sense takes to cover this distance is $t_1 = l/(c - v)$. The corresponding time t_2 for light travelling in the opposite sense is $t_2 = l/(c + v)$. The difference Δt between these times is

$$\Delta t = t_1 - t_2 = \frac{l}{c - v} - \frac{l}{c + v} = \frac{2lv}{c^2 - v^2}.$$

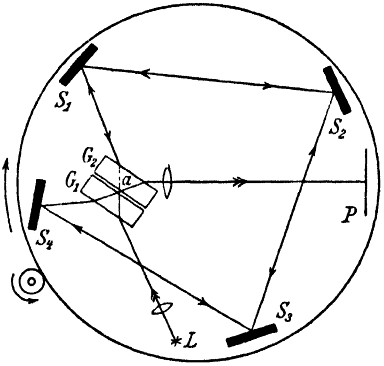

Fig. 9.—Sagnac's experiment

Neglecting v^2 in comparison with c^2, we may write $\Delta t = 2lv/c^2$. When $v = 0$, we have $\Delta t = 0$, i.e. the time is the same for either sense. When $v \neq 0$, the time difference causes a displacement of the interference fringes. If the path difference is just one wave-length λ (i.e. if Δt is just equal to one period λ/c), the system of fringes is displaced by one fringe. Hence the path difference expressed in wave-lengths (or the displacement of the interference pattern expressed in fringes) is

$$\Delta\lambda = \frac{2lv}{c^2} \div \frac{\lambda}{c} = \frac{2l}{\lambda}\frac{v}{c}.$$

The effect is thus of the first order. An actual element of path-length l_i which makes an angle ϕ_i with the direction of rotation has the component $l_i \cos\phi_i$ in this direction. Since v, the linear velocity of rotation of the system at this point, is given by $v = r_i\omega$, where ω is the angular velocity and r_i the distance from the axis of rotation, the corresponding path difference is

$$\Delta\lambda_i = \frac{2l_i \cos\phi_i r_i \omega}{\lambda c} = \frac{2\omega}{\lambda c} l_i r_i \cos\phi_i.$$

Summing over the whole optical path, we obtain the total path difference due to the rotation of the system, namely

$$\Delta\lambda = \frac{2\omega}{\lambda c}\Sigma l_i r_i \cos\phi_i.$$

But

$$\Sigma l_i r_i \cos\phi_i = 2S,$$

where S is the area of the surface enclosed by the optical path. Hence

$$\Delta\lambda = \frac{4\omega S}{\lambda c},$$

or, if $p = \omega/(2\pi)$ is the number of revolutions per second,

$$\Delta\lambda = \frac{8\pi p S}{\lambda c}.$$

The experiment was carried out by Sagnac in 1914, using $p = 1$-2 revolutions per second, $S = 865$ sq. cm. and $\lambda = 436\ m\mu$. The positions of the fringes were compared for opposite directions of rotation, so that the effect was doubled, as compared with the procedure in which the position of the fringes with the system at rest is taken as reference point. The method adopted also eliminated effects due to changes of shape resulting from the centrifugal forces set up by the rotation. The observed displacements were of the order of 0·05 of the distance between successive fringes. Similar experiments have recently been carried out with increased accuracy by Pogany. The results are in good agreement with the formula given above.

According to what was said on p. 430, the results of experiments of this kind involving first-order effects must remain unaffected by the presence of a material medium. In a medium of refractive index μ the velocities of propagation of the two oppositely-directed rays are

$$c' = \frac{c}{\mu} \pm \left(1 - \frac{1}{\mu^2}\right)v.$$

Relative to the moving medium, therefore, the velocities must be

$$c' \mp v = \frac{c}{\mu} \mp \frac{v}{\mu^2}.$$

Hence we have, as above,

$$\Delta t = \frac{l}{\frac{c}{\mu} - \frac{v}{\mu^2}} - \frac{l}{\frac{c}{\mu} + \frac{v}{\mu^2}} = \frac{2l\frac{v}{\mu^2}}{\frac{c^2}{\mu^2}} = \frac{2lv}{c^2}.$$

Thus the result is the same as in the absence of a material medium.

Experiments with a medium present are very difficult from the technical point of view, but have been carried out by HARRESS (1912) and POGANY (1928). The results obtained are in good agreement with the theory.

In 1925 MICHELSON * and GALE performed a similar experiment, using the *rotation of the earth.* Owing to the smallness of p, it was necessary to make S very large in order to obtain a measurable effect. A rectangle 613 metres by 340 metres ($S = 2{\cdot}1 \times 10^9$ sq. cm.) was used. For obvious experimental reasons this rectangle had to be horizontal, so that only the projection at right angles to the earth's axis was effective. (The experiment was carried out in latitude 42°.) A further difficulty arises from the fact that it is impossible to stop or reverse the earth's rotation and obtain a reference position for the measurement of fringe displacements. To overcome this, use was made of an auxiliary optical path enclosing so small an area that the effect in it was negligible (see fig. 10). In order to prevent undesirable disturbances, the light was made to travel through evacuated tubes. The observed displacement of 0·24 of a fringe is in agreement with the SAGNAC formula.

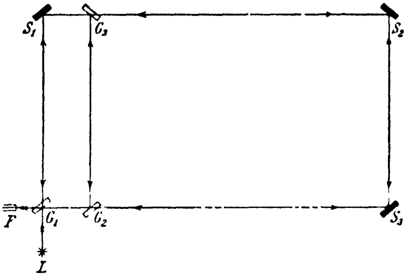

Fig. 10.—Diagram of the earth-rotation experiment of Michelson and Gale

The Interference Experiment of the Second Order (the so-called Michelson Experiment).—No first-order effect (i.e. no effect proportional to v/c) can be observed when the light source, apparatus, and observer all have a common uniform rectilinear motion and the optical path is a closed one (in the limit, runs to and fro between two points). For if l is the path-length in the direction of motion, the times taken by the light in the two senses are $l/(c \mp v)$ and the total time is therefore

$$\frac{l}{c - v} + \frac{l}{c + v} = \frac{2cl}{c^2 - v^2}.$$

The corresponding total time when the system is at rest is $2l/c$. The time difference Δt introduced by the motion is therefore

$$\Delta t = \frac{2cl}{c^2 - v^2} - \frac{2l}{c} = \frac{2lv^2}{c(c^2 - v^2)} \sim \frac{2l}{c}\left(\frac{v}{c}\right)^2,$$

which is of the second order of smallness. It was shown on p. 431

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* ALBERT ABRAHAM MICHELSON, born at Strelno (Posen), was professor at Chicago, received the Nobel Prize in 1907, died in 1931 (see Vol. II, pp. 190, 201, 209, 217).

that this result is unaffected by the presence of a material medium. As was pointed out as early as 1878 by MAXWELL, experiments on the influence of uniform rectilinear motion can only be expected to show effects of the second order, i.e. effects proportional to $(v/c)^2$. Owing to the smallness of v, such effects must be very much smaller than first-order effects and hence must ordinarily be beyond the limits of observation. Cosmic velocities of several kilometres per second must be investigated if an appreciable effect is to be hoped for.

The simplest suitable apparatus is the MICHELSON interferometer, the principle of which has been described in Vol. IV, p. 190. For the method of producing interference fringes with the reflecting mirrors at equal distances from the separating plate, as in the present application, see Vol. IV, p. 193. We shall now consider the case (fig. 11) in which the interferometer is moving in the plane of the figure with the velocity v. The direction of motion (as indicated in the figure) is parallel to the one arm of the instrument and at right angles to the other.

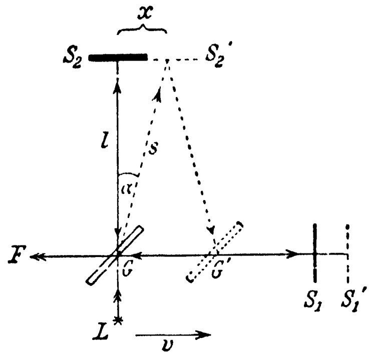

Fig. 11.—Diagram of Michelson's experiment (absolute rays shown dotted)

Consider first the arm GS_1, which is parallel to the direction of motion. If the length GS_1 is l, the total time t_p which light takes to pass from G to S_1 and back is (as above)

$$t_p = \frac{l}{c-v} + \frac{l}{c+v} = \frac{2lc}{c^2-v^2} = \frac{2l}{c}\,\frac{1}{1-\dfrac{v^2}{c^2}}.$$

Since v/c is very small compared to unity, we may therefore write

$$t_p = \frac{2l}{c}\left(1+\frac{v^2}{c^2}\right).$$

We now consider the other arm GS_2, which is at right angles to the direction of motion. Here too the motion causes an alteration of the time taken by the light to pass from G to S_2 and back, as compared with the time taken when the system is at rest. For in the time t_p the point G of the dividing plate, as judged by an observer not sharing the motion of the apparatus, has moved to G′ (see figure). The light travelling along the arm GS_2 therefore traces out two sides of an isosceles triangle, each of length s, the angle between them being twice the angle of aberration α (given by $\sin\alpha = v/c$). Let the length of the base GG′ of this isosceles triangle be $2x$. Then each side is given by

$$s^2 = l^2 + x^2.$$

Since $x = s\sin\alpha = sv/c$, we have

$$s^2 = l^2 + \frac{v^2}{c^2}s^2,$$

whence

$$s = \frac{l}{\sqrt{1-\dfrac{v^2}{c^2}}} \sim l\left(1+\frac{1}{2}\frac{v^2}{c^2}\right).$$

The time t_s taken by the light in its double journey along this arm is therefore

$$t_s = \frac{2l}{c}\left(1+\frac{1}{2}\frac{v^2}{c^2}\right).$$

The difference Δt between the times for the two arms of the instrument is obtained by subtraction, namely

$$\Delta t = t_p - t_s = \frac{2l}{c}\left(1+\frac{v^2}{c^2}\right) - \frac{2l}{c}\left(1+\frac{1}{2}\frac{v^2}{c^2}\right) = \frac{l}{c}\frac{v^2}{c^2}.$$

This time difference means that the two beams combine at the dividing plate with their phase difference altered from the value which it has when the whole system is at rest. Hence the motion of the system may be expected to cause a displacement of the interference fringes. The displacement, expressed in terms of the distance between successive fringes (i.e. the path difference expressed in wave-lengths) will be

$$\Delta\lambda = \Delta t \Big/ \frac{\lambda}{c} = \frac{l}{\lambda}\frac{v^2}{c^2}.$$

An important case is that in which the velocity v of the whole system is maintained indefinitely; for then it is not possible to compare the position of the interference fringes with their position when the system is at rest. This difficulty can be overcome, however, by mounting the whole apparatus so that it can be turned about an axis. Rotation through 45° from the position represented in fig. 11 brings both arms into the same inclination to the direction of motion, so that by symmetry the effects will be the same for both and will just balance one another. This position can therefore be used for the desired comparison. Moreover, if the apparatus is rotated through a further 45° (i.e. through 90° in all), the arm which was originally parallel to the direction of motion will be brought into a position at right angles to this direction, and the arm which was originally at right angles to the direction of motion will be brought into a position parallel to this direction. Hence the displacement of the fringes relative to the intermediate setting will be reversed. Thus rotation of the apparatus through 90° must double the effect.

Up to the present it has not been possible to carry out this so-called *Michelson experiment* for motions of the apparatus relative to the earth's surface. The experimental difficulties in eliminating disturbing effects due to vibration, temperature variations, &c., are too great. For the experiments of this kind using the motion of the earth in space see p. 442.

2. The Effect of Motion on Statical Electric and Magnetic Fields

First-Order Effects.—Every electric charge moving with the velocity v is associated with a magnetic field of strength proportional to v/c. This has been discussed in Vol. III, and special reference may be made to the experiments of RÖNTGEN, ROWLAND, and EICHENWALD described there (Vol. III, p. 164 *et seq.*). The magnetic field which is produced by the motion of electric charges is observable by an observer at rest relative to the earth's surface, and the field strength is proportional to the relative velocity of the charges with respect to this observer. On the other hand, the motion of a *magnetic* field is associated with the production of an electric field which is at right angles both to the direction of motion and to the magnetic lines of force (see Vol. III, fig. 8, p. 164) and whose field-strength is proportional to the relative velocity of the magnetic field with respect to the observer. This electric field has been demonstrated experimentally by H. A. WILSON (1904) and W. WIEN (1914). The effect is determined only by the relative velocity of the magnetic field with respect to the observer (see further p. 451), and for technical reasons the magnetic field in these experiments was kept at rest relative to the earth and the observer (test body) was made to move. In WILSON'S experiment an insulated hollow cylinder whose surfaces were coated with metal was rotated in a magnetic field. As a result of the rotation, the surface of the cylinder became electrically charged. W. WIEN shot luminous positive rays of hydrogen with a velocity of about 500 kilometres per second through a magnetic field of about 14,000 ampere-turns per centimetre. Owing to the motion relative to the magnetic field, an electric field is superimposed on the fields of the atoms (p. 451), and the wave-length of the light emitted is altered by the Stark effect. The magnitude of the observed Stark effect forms a measure of the strength of the electric field involved. The experiments showed that the electric field-strength E is indeed proportional to the relative velocity v of the charged particles with respect to the magnetic field, namely $E = v_{\perp} H/c$. The effect is of the first order.

Simultaneous Motion of Field and Observer.—In the above experiments the conditions of motion are quite analogous to those in the previously-described optical experiments which exhibit a first-order effect. It is possible, however, to arrange the experiments so that the whole system (including the observer) is in motion. In optical experiments of this kind no first-order effect can be observed. H. A. Lorentz has shown that, according to Maxwell's equations, first-order effects must likewise be absent in experiments on statical or stationary electric and magnetic fields, because of the exactly-compensating effects of the motion upon the test body itself (see p. 451). Accordingly, it is impossible (so far as first-order effects are concerned) for an observer to demonstrate the magnetic field produced by the motion of a charged condenser, if the observer himself shares in that motion. This is completely analogous to the optical case. Up to the present, experiments of this kind have not been carried out with motions relative to the earth's surface.

The Trouton-Noble Experiment.—Just as in optical experiments, effects of the second order may be expected in experiments on electric and magnetic fields. The greatest sensitiveness is attainable with an apparatus in which the turning moment acting upon a plate condenser is determined. This arrangement was first suggested by Fitzgerald, and the experiment was first performed by Trouton and Noble, using the motion of the earth (p. 443).

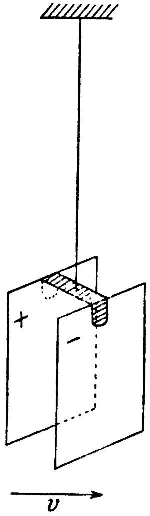

Fig. 12.—Diagram of the experiment of Trouton and Noble.

A plate condenser is suspended (fig. 12) so as to be free to turn about an axis parallel to the plane of the plates. Fig. 13 shows the condenser as seen from above. Let A be the area of each plate, s the distance between the plates, σ the surface density of charge, and K the dielectric constant of the medium. Motion of the condenser at right angles to the lines of force of the field between its plates produces a magnetic field of strength H and energy density $S_m = \frac{1}{2}\mu\mu_0 H^2$ (Vol. III, p. 429), where $\mu\mu_0$ is the absolute permeability of the dielectric (Vol. III, p. 404). But $H = \sigma v$, where v is the velocity of motion. Hence $S_m = \frac{1}{2}\mu\mu_0\sigma^2 v^2$. The total energy of the magnetic field in the space of volume As between the plates is

$$E_m = \tfrac{1}{2}\mu\mu_0\sigma^2 v^2 As.$$

Now the capacity C of the condenser is given by $C = KK_0A/s$ (see Vol. III, p. 84), where K_0 is the fundamental electrostatic constant. Hence if Q is the charge on the condenser and U the potential difference between its plates, we may write

$$\frac{Q}{U} = C = \frac{KK_0A}{s},$$

whence

$$\sigma = \frac{Q}{A} = \frac{KK_0U}{s}.$$

Substituting this in the expression for E_m obtained above, we have

$$E_m = \frac{\mu\mu_0 v^2 AK^2K_0{}^2U^2}{2s}.$$

The electrostatic energy of the condenser is given (Vol. III, p. 96) by $E_e = \frac{1}{2}KK_0E^2As$. Hence, since $E = U/s$, we have

$$E_e = \frac{KK_0U^2A}{2s}.$$

Combining the expressions for the magnetic and electrostatic energies, we obtain the relation

$$E_m = \mu\mu_0KK_0E_e v^2.$$

In Vol. III, p. 616, it is shown that $\mu_0K_0 = 1/c^2$. Hence

$$E_m = \mu KE_e \frac{v^2}{c^2}.$$

If the direction of motion of the condenser, instead of being parallel to the plates (as assumed above), is inclined to the plates at the angle ψ (see fig. 13), then $v \cos\psi$ must be substituted for v in the above. We then have

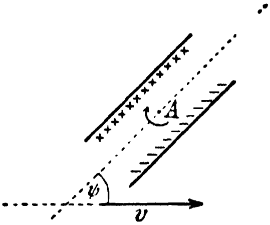

Fig. 13.—Plan of apparatus shown in fig. 12

$$E_m = \mu KE_e \frac{v^2}{c^2} \cos^2\psi.$$

The total energy E (magnetic and electrostatic) is therefore

$$E = E_e\left(1 + \mu K \frac{v^2}{c^2} \cos^2\psi\right).$$

Since this total energy tends to become as small as possible, $\cos\psi$ tends to become zero, i.e. ψ tends to become 90°. Thus there is a tendency for the condenser to set itself with its plates at right angles to the direction of motion.

The change of energy dE due to a rotation through $d\psi$ is given by the equation $dE = -R\,d\psi$, where R is the turning moment and the negative sign takes account of the fact that an increase of ψ corresponds to a decrease of E. Hence, since E_e is independent of ψ, we have

$$R = -\frac{dE}{d\psi} = \mu K E_e \frac{v^2}{c^2} 2\cos\psi\sin\psi$$

$$= \mu K E_e \frac{v^2}{c^2} \sin 2\psi.$$

The moment is therefore a maximum when $\sin 2\psi$ is a maximum, i.e. when $2\psi = 90°$ or $\psi = 45°$. The effect is seen to be of the second order, i.e. proportional to v^2/c^2.

An experiment of this kind using motion relative to the earth's surface has not yet been carried out, owing to the enormous experimental difficulties. For experiments on the motion of the earth in space see p. 442.

3. The Problem of Absolute Motion

According to well-founded classical views, the propagation of light and the electromagnetic coupling between the fields involved are effected by the universal ether, the medium of electric and magnetic (and probably also gravitational) phenomena. The space round an electrically charged body, for instance, is supposed to be in a peculiar state of excitation (the electrical state—presence of an electric field), and we can ascribe to every point a measure of this state (e.g. field-strength or energy-density). This means that the individual points of the space differ from one another in a definite quantitative manner. Hence we must suppose that the space is filled with some substance which is capable of assuming the different states at different points; but we have already seen, in Vol. I, p. 3, that this substance must not be thought of as being material. Following upon the recognition of the undulatory nature of the propagation of light, the most plausible assumption was made that the ether is at rest in space and fills all space uniformly. The heavenly bodies, such as the earth itself, were assumed to move through the ether without resistance.* According to this view, we are justified in asking the question: what is the relative velocity of a body on the earth's surface with respect to this ether at any moment, i.e. what is the " absolute " velocity of the body? The earth itself undoubtedly moves through space. It possesses a velocity of about 30 kilometres per second in virtue of its orbital motion round the sun. Then the sun has a velocity of about 19 kilometres per second relative to the nearer fixed stars and directed towards the constellation of Hercules. In addition, there is a velocity of several hundred kilometres per second relative to the star-clusters. Even if the velocity of the earth relative to the ether happened to be zero at one moment, it must certainly alter in the course of a year, owing to the earth's orbital motion round the sun. Thus an absolute velocity of at least 30 kilometres per second is to be expected at the earth's surface at some season of the year.

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* This is not so difficult to imagine in the light of more recent views upon the structure of matter, according to which matter is regarded as the effect of ether-processes related to electromagnetic processes, i.e. as ether in a special form. To choose a rough simile, the behaviour of matter when moving relative to the ether is rather like that of a cloud resting on a mountain peak. The shape and position of the cloud may remain practically unchanged, even although there is a strong wind.

Accordingly, electromagnetic experiments upon the earth's surface may be expected to show the effects of this absolute motion, as discussed in the preceding sections. We are led to the idea of an " ether wind " in the laboratory. If the direction of this wind is not parallel to the earth's axis, it will vary as a result of the earth's daily rotation; again, if it is not parallel to the axis of the earth's orbit, it will vary as a result of the earth's motion round the sun. At some time or other, therefore, we must expect it to have a demonstrable velocity. Here, of course, we are concerned with experiments in which both observer and apparatus are moving together, i.e. are at rest relative to one another. Hence, according to the preceding discussions, only second-order effects (i.e. effects proportional to $(v/c)^2$) are to be anticipated. It is not surprising, therefore, that negative results were obtained in many experiments carried out with the greatest care during the last century, in the hope of finding first-order effects. The only conclusive experiments are those which deal with effects of the second order: in particular the MICHELSON-MORLEY experiment and the TROUTON-NOBLE experiment.

The Michelson-Morley Experiment.—The principle of this experiment (Michelson experiment) has been given on p. 435. The procedure is to rotate the whole apparatus at various times of day and at various seasons of the year and to look for a displacement of the interference fringes. The displacement must be periodic as the apparatus is rotated, the period corresponding to rotation through 180°. The first experiments were carried out in 1880–1 by A. A. MICHELSON in the Physics Institute of Berlin University and later in Potsdam. The expected displacement for an absolute velocity of 30 kilometres per second (orbital velocity of the earth) was 0·04 of the distance between successive fringes. The observed displacements (probably due for the most part to elastic and thermal disturbances) were only 0·004 to 0·015. The experiments were repeated with very great care by MICHELSON and MORLEY in Cleveland (July, 1887). The optical apparatus was mounted on a block of sandstone floating in mercury, so that the whole system could be rotated without serious vibration during the course of the observations (fig. 14). An optical path of 11 metres was obtained by repeated reflections to and fro across the block. The observed fringe displacements correspond to an ether wind of only 8 kilometres per second. The investigations have been continued with improved apparatus by MORLEY and MILLER (1902–6) and with extreme care by MILLER (from 1921 onwards). Repetitions of the very difficult experiments have also been carried out by TOMASCHEK (1924), KENNEDY (1926–8), PICCARD and STAHEL (1926–8), ILLINGWORTH (1928), MICHELSON, PEASE, and PEARSON (1929), using modified experimental arrangements. Measurements with a very refined apparatus have also been made by JOOS (1930). MILLER, whose investigations are the most extensive, comes to the conclusion that there is a demonstrable ether wind with a velocity of 10 to 11 kilometres per second, this being about one-twentieth of an " absolute velocity " of the earth (208 kilometres per second) directed towards a point situated in the Great Magellanic Cloud, about 7° from the pole of the ecliptic at right ascension 5 hours and declination —70°. The last investigation of MICHELSON (1929) gives 6 kilometres per second as the upper limit of the velocity of the ether wind. Considerably smaller effects are obtained by the other observers, the limit being about 1 to 2 kilometres per second. TOMASCHEK has shown that the experiment gives the same result when light from planets or fixed stars is used.

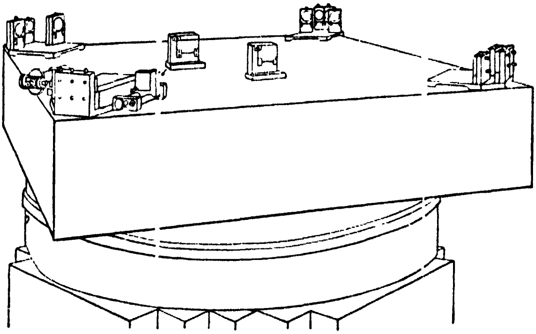

Fig. 14.—The apparatus used in the Michelson-Morley experiment (1887)

Summing up the result of all the investigations, we may make the following statement:

Experiments with the Michelson interferometer certainly do not show the full " absolute motion " of the earth. Probably no " absolute motion " at all is demonstrable in this way.

The Trouton-Noble Experiment.—This experiment, the principle of which has been explained on p. 439, was first carried out in 1904 by TROUTON and NOBLE. It has been repeated a number of times by TOMASCHEK, using improved apparatus. Experiments of this kind can be made more sensitive than the MICHELSON-MORLEY experiment. The results (see fig. 15) indicate that, even at a height of 3500 metres above sea-level, there is *no effect* corresponding to an ether wind of more than ½ kilometre per second.

Electrical methods also fail to demonstrate any " absolute motion " of the earth.

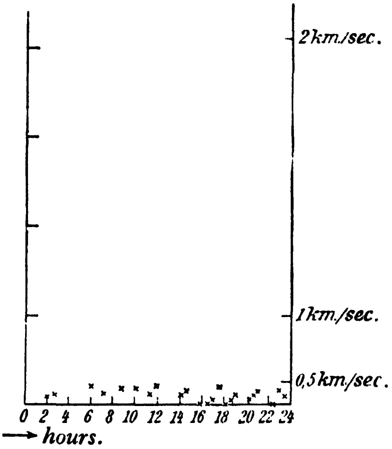

Fig. 15.—Results of the Trouton-Noble experiment performed at a height of 3500 metres above sea-level (after Tomaschek)

Conclusion from Experiments on the " Absolute Motion " of the Earth.—Both the above decisive experiments show (at least to a first approximation) that there is *no ether wind* at the earth's surface, i.e. that there is no demonstrable relative motion of the apparatus and observer with respect to the ether. From this we may conclude that:

The surface of the earth is at rest relative to the ether. It carries the surrounding ether along with it.

Thus an observer in a terrestrial laboratory is at rest relative to the medium in which electric and magnetic processes take place. In all directions and at all times, therefore, the velocity of light is c relative to the earth's surface. For the rotational motion of the earth see p. 446.

Experiments concerning the Effect of the Earth's Motion on the Force of Gravity.—It is conceivable that, although electromagnetic phenomena are not influenced by the motion of the earth, for the reasons given above, such an influence might be observable in the case of gravitation (see p. 445). Experiments on this matter have been carried out by Tomaschek and Schaffernicht, who determined the variation of the force of gravity with time. Their measurements were accurate to 10^{-9} of the quantity measured. Fig. 16 is a reproduction (on a reduced scale) of a photographic record showing the diurnal variations, which can be completely explained as due to the influence of the moon and the sun. The effect of the absolute motion of the earth upon the force of gravity, which would be apparent as a regular periodic variation with a period equal to the unit of sidereal time, must certainly amount to less than 10^{-8}.

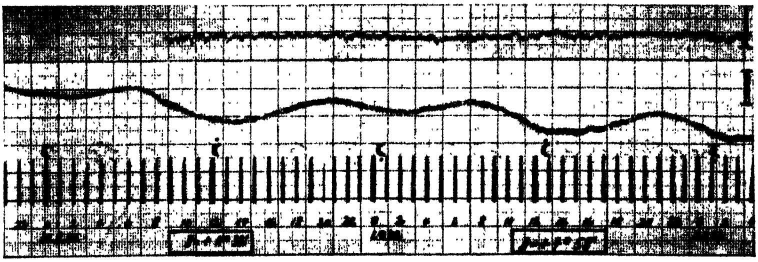

Fig. 16.—Variation of the force of gravity with time (photographic record, after Tomaschek and Schaffernicht)

Thus the motion of the earth in space has no appreciable effect on gravity.

The Carrying-along of the Ether by the Earth.—The conclusion that the earth carries the ether along with it (or, perhaps better expressed, that near the earth's surface electromagnetic phenomena take place relative to the earth) appears at first sight to be contradicted by the experiment of LODGE (p. 429), who was unable to detect any carrying-along of the ether in the neighbourhood of moving bodies, and also by the negative results of experiments designed to demonstrate the carrying-along of the ether in the interior of moving media.

It was shown by LENARD, however, that the conclusion referred to can be brought into harmony with all the experimental facts. Indeed, the view appears a very satisfactory one in the light of our more recent knowledge of the structure of matter. We know that matter is principally, and probably exclusively, electromagnetic in character. The fields of force involved extend far out into space. These fields, and consequently matter itself, are processes in the ether associated with extraordinarily large concentrations of energy. It is therefore quite in harmony with our views on the nature of matter to assume that every body carries along *its own* ether in its neighbourhood, just as it carries along its own gravitational field which, as is suggested by the inertia of energy (p. 223), is probably bound up with its electromagnetic fields. On the average, therefore, the state of the ether at any particular point in space is determined by the surrounding matter. To make things more precise, we may think of the effect of a given mass of matter as measured by the strength of its gravitational field. Near the earth's surface, then, the preponderant effect is that due to the whole mass of the earth. We are led to conclude that large cosmic bodies must carry along the ether within a considerable radius. As a result, electromagnetic processes in the neighbourhood of such a large body must take place relative to it: the velocity of light, for instance, is c relative to the body. At greater distances in space the proper ethers of the individual bodies become mixed: possibly in such distant regions there is an "ultimate ether" *, i.e. an ether which fills space independently of matter.

As was mentioned above, LENARD has shown that these views are in harmony with all the experimental facts. The negative results of the MICHELSON-MORLEY and TROUTON-NOBLE experiments are self-evident, since in both cases the whole system is at rest relative to the ether. Nor does aberration, considered as a pure inertial phenomenon, present any difficulties. The explanation in terms of an ether which is carried along by the earth is the simplest and most natural one for the data so far accumulated, and must therefore be regarded as the best explanation at present available.

The *positive* result of the MICHELSON-GALE experiment (p. 435) proves that *the ether does not share in the rotation of the earth.* If the observations are correct (the experiment has not been repeated by other workers), there must be at the earth's surface an ether wind with a velocity of the order of several hundred metres per second (according to the geographical latitude). With the exception of this experiment, the measurements so far made are not sufficiently accurate; but with the means now available it should perhaps be possible to decide this point by means of a second-order experiment. Some of the first-order experiments which have been carried out have attained a sufficient accuracy, in particular the experiment designed to detect the magnetic field of a condenser (the so-called RÖNTGEN experiment). As carried out by TOMASCHEK (at a height of 3500 metres above sea-level) this had a limit of error of 20 metres per second. According to what has been said above, however, the negative result of these first-order experiments is not conclusive. The negative result of the RÖNTGEN experiment, together with the positive result of the MICHELSON-GALE experiment, may, however, be taken as experimental evidence supporting LORENTZ's deduction (p. 439) that first-order effects must be absent in electrostatic experiments.

The conclusions of MILLER (p. 443), that his repetitions of the MICHELSON-MORLEY experiment show a small effect due to a relatively large absolute velocity, can readily be brought into line with the views developed here.

The So-called Lorentz Contraction.—The failure of experiments to detect an absolute motion of the earth has been explained above by assuming that the earth carries the ether along with it. This assumption (in a somewhat different form) was put forward very early: in the middle of the nineteenth century its chief supporter was STOKES. At that time, however, it led to difficulties and could not yield satisfactory results, because the ether was thought of as possessing too material a character, being supposed to have the properties of a gas, a liquid, or a solid, or even of all three simultaneously. It was a difficult matter to represent the motion of the heavenly bodies through this medium in such a way as to account satisfactorily for the phenomenon of aberration, which requires an irrotational motion of the medium. Nowadays these difficulties have disappeared in the light of our knowledge that the ether, as the medium of electromagnetic phenomena, is subject to laws (describable in larger regions by MAXWELLS' equations and in smaller regions by the quantum electrodynamics which is at present in course of construction) quite different from those of the particular modification of the ether which we call matter.

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* Ger. *Uräther*: the name is due to LENARD.

In the latter half of the nineteenth century, however, the difficulties involved in the idea of a carrying-along of the ether (supposed to be material) appeared to be so great that preference was given to the idea of an ether at rest in space, i.e. of the existence of an ether wind at the earth's surface. Even at this time numerous experiments had been carried out with the object of demonstrating this ether wind, and had all given negative results. This was quite in harmony with the current view; for LORENTZ showed that the experiments (all of which were of the first order) must be quite unaffected by an ether wind of the kind sought for, at least so far as first-order effects are concerned. Thus there was no evidence against the idea of the ether being at rest in space, and this became generally accepted. Not until the unexpected negative result of the MICHELSON-MORLEY experiment, which was of the second order, did serious difficulties arise. Nevertheless, the current materialistic views about the ether were so firmly rooted that it was considered necessary to reject the solution which assumes that the ether is carried along by the earth. Although this assumption is now quite natural, the historical development of the subject is a most potent factor in current opinion.

How is it possible for the MICHELSON-MORLEY experiment to give a negative result in spite of an ether wind? An answer to this question was given by FITZGERALD * in 1891. Since there is no doubt that the distribution of the fields of force is affected (p. 228), the forces holding a body together may be altered by the motion of the body through the ether. FITZGERALD suggested that this alteration may be such as to cause a shortening of that arm of the Michelson apparatus which is parallel to the direction of motion, the extent of the shortening being exactly sufficient to counteract the extra time which the light would take in consequence of the ether wind (p. 437). In 1895 LORENTZ worked out this idea systematically, and this shortening of all lengths

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* GEORGE FRANCIS FITZGERALD (1851–1901), Professor of Natural Philosophy at Trinity College, Dublin.

as a result of motion is usually referred to as the *Lorentz contraction.*

Every length l in the direction of motion is supposed to be shortened to $l\sqrt{1-(v^2/c^2)}$. Hence in the calculation of p. 436 the length of the arm GS_1 must be equated to this expression, whereas the length $2s$ (which is approximately at right angles to the direction of motion) is altered by only a negligible amount. Hence we have

$$t_p = \frac{2l}{c\sqrt{1-\frac{v^2}{c^2}}} = \frac{2l}{c}\left(1+\frac{1}{2}\frac{v^2}{c^2}\right) = t_s.$$

The times taken by the light to travel to and fro along the two arms are thus equal, and no displacement of the interference fringes as compared with the case in which the apparatus is at rest is to be observed. (See p. 454.)

Experimental Decision between the Two Alternative Theories.—It is possible in principle, to decide between the two alternative views (*a*) that the ether is carried along by the earth and (*b*) that the ether is everywhere in a state of absolute rest. The decision could be obtained by carrying out an experiment of the second order (e.g. the Michelson experiment) with a system moving relatively to the earth's surface. If the first view is correct, such an experiment must give a positive result; if the second view is correct, the result must be negative. In the present state of our knowledge we cannot predict what the result will be, and the performance of the experiment is for the time being technically impossible. We may adopt the assumption that the ether is carried along by the earth, both because of its greater simplicity and also because the other alternative presents certain difficulties which will be discussed below.

The Relativity Principle.—It is unsatisfactory that (as has been shown by LAUE) the assumption of a Lorentz contraction is not sufficient by itself to account for the negative result of the Trouton-Noble condenser experiment: it is necessary to make the additional assumption that the electrostatic forces are affected in a certain way by the motion. The idea of the earth carrying along the ether being thought untenable for the reasons mentioned on p. 447, this unsatisfactory state of affairs demanded a new kind of explanation. A solution of the difficulty was given by EINSTEIN * in his so-called *relativity*

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* ALBERT EINSTEIN, a German-Swiss, born in 1879 in Würtemberg of Jewish parents. After holding a post as teacher of mathematics and physics at the Polytechnic School of Zürich, he became an examiner of patents in Berne from 1901 to 1909. During this time he took his Doctorate at the University of Zürich, and on the merit of his research was appointed extraordinary professor of theoretical physics there. In 1911 he went to Prague as professor of physics, but returned the next year to the Zürich Polytechnic. His work attracted so much attention that in 1913 he was made Director of the Kaiser-Wilhelm Institut at Berlin. Since 1933 he has been in the U.S.A. as professor of mathematics at the Institute for Advanced Study in Princeton. His well-known work upon the theory of relativity was commenced in 1905, the so-called special theory of rela-

theory. He attempted to construct a consistent representation of the electrodynamics of moving media on the basis of two fundamental postulates: (1) The velocity of light as measured in a vacuum is always c, no matter what the state of motion of the observer. (2) The principle of relativity is a completely universal law of nature. Before discussing the second postulate, we must inquire briefly into the nature of the principle of relativity, which is of importance even in classical mechanics.

Consider a ball which is thrown upwards by a person travelling in a railway carriage with uniform velocity along a straight track. As observed by the person in the carriage the motion of the ball is just the same as if the carriage were at rest. When the ball is thrown vertically upwards, it is observed to fall vertically downwards again. Although the track of the ball is a straight line, as viewed by the person in the carriage, as viewed by a person standing beside the railway line it is a parabola. This latter observer could photograph the parabola and hence determine the velocity of the train relative to the ground. On the other hand, the observer who is travelling in the train cannot possibly deduce anything about his own uniform rectilinear motion from the behaviour of the ball. As a fact of experience, there is no mechanical process at all by which he could detect this motion.

But whenever the train goes round a curve or has its velocity accelerated or retarded, the ball no longer falls vertically downwards. Non-uniform motion can thus be detected by observations carried out within the moving system. Hence the **relativity principle of mechanics** only holds for uniform motion in a straight line:

The uniform rectilinear motion of a system cannot be detected by means of any mechanical process taking place within the system.

A mechanical process may be represented quantitatively with the help of a system of co-ordinates (so-called frame of reference) connected rigidly with the observer. The principle of relativity may then be expressed in the following form: *All the laws of mechanics are entirely unaffected by a uniform rectilinear motion of the system of co-ordinates to which they are referred.*

Suppose that the person in the train throws the ball forward with the velocity u (relative to himself) in the direction of motion of the train. As observed by the person standing beside the line, relative to whom the train is moving with the velocity v, the velocity of the ball is $v + u$. This is an instance of the so-called **composition of velocities,** which has been discussed at length in Vol. I, p. 37.

tivity being followed up in 1915 by the general theory and in 1929 by the unified field theory, the latter being an attempt to construct a mathematical formulation covering the laws of electromagnetism and of gravitation. He has also made important and fundamental contributions to many other departments of physics, including the theory of the Brownian movement, the photoelectric effect, and the variation of specific heat with temperature. EINSTEIN is widely acknowledged to be one of the most brilliant of living theoretical physicists, and received the Nobel Prize in 1921.

An example may be given to illustrate the applicability of the relativity principle in mechanics. Consider two elastic spheres of masses m_1 and m_2, moving with the velocities u_1 and u_2 respectively in the x-direction of a certain frame of reference. Suppose that the spheres collide, and let the velocities after the collision be respectively v_1 and v_2. Then by the principle of the conservation of energy we have

$$\tfrac{1}{2}m_1u_1^2 + \tfrac{1}{2}m_2u_2^2 = \tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2.$$

Now consider the process relative to a frame of reference which is moving with the velocity V relative to the first, and also in the direction of its x-axis. According to the principle of the composition of velocities, the velocities relative to this new frame of reference are respectively $u_1 - \mathrm{V}$, $u_2 - \mathrm{V}$, $v_1 - \mathrm{V}$, and $v_2 - \mathrm{V}$. Now the relativity principle states that the principle of the conservation of energy is still valid for moving frames of reference, so that we must have

$$\tfrac{1}{2}m_1(u_1 - \mathrm{V})^2 + \tfrac{1}{2}m_2(u_2 - \mathrm{V})^2 = \tfrac{1}{2}m_1(v_1 - \mathrm{V})^2 + \tfrac{1}{2}m_2(v_2 - \mathrm{V})^2.$$

Subtracting the equation previously obtained, we arrive at the relation

$$m_1u_1 + m_2u_2 = m_1v_1 + m_2v_2.$$

But this is the principle of the conservation of momentum. Thus from the principles of the conservation of energy and momentum in the first frame of reference it follows that the principle of the conservation of energy must also hold for the second frame of reference, as is required by the relativity principle.

Relativity of Electromagnetic Processes.—As has been pointed out on a number of previous occasions, electromagnetic effects are also determined solely by relative motion.

We shall consider this in more detail in the particular case of W. Wien's experiment (p. 438). Imagine a particle with an electric charge at rest relative to the ether, and let a magnetic field (e.g. that of a bar magnet) be moved past it (fig. 17). Owing to its motion through the ether, the magnet is surrounded by a rotational electric field in addition to its own magnetic field. The electric field in the neighbourhood of the charged particle is therefore modified by the motion of the magnet. In the particular case of an atom, this modification can be detected by means of the Stark effect on the light emitted by the atom. The two electric fields—that of the charged particle and that of the moving magnet—give rise to a mechanical interaction. The electric field of the magnet urges the charged particle up out of the plane of fig. 17. By the principle of action and reaction the magnet is subjected to a turning moment which tends to urge the N-pole down through the plane of fig. 17 and the S-pole up out of this plane. These forces acting upon the magnet mean that there must be a magnetic field superimposed upon that of the magnet itself.

Now consider the same relative motion, but this time (fig. 18) let the magnet be at rest relative to the ether and let the charged particle be moved past it as shown. On account of its motion the electric charge is surrounded by a rotational magnetic field which tends to urge the N-pole of the magnet down through the plane of the figure and the S-pole up out of this plane. By the principle of action and reaction, the charged particle is acted on by a force urging it up out of the plane of the figure. This means that there must be an electric field superimposed on that of the charge itself. In the case of an atom this modification of the electric field can be detected by the Stark effect on the light emitted by the atom, and it is this effect that W. Wien measured in his experiment.

We see that the interaction between charged particle and magnet is the same in both cases. This interaction is determined solely by the relative motion.

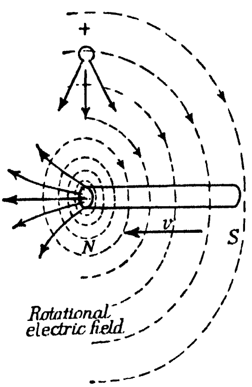

Fig. 17.—Interaction between a moving magnet and a charged particle at rest.

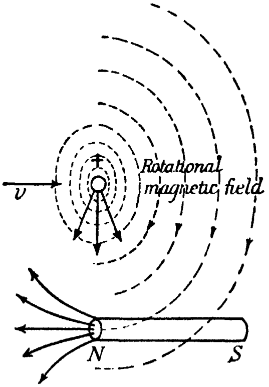

Fig. 18.—Interaction between a moving charged particle and a magnet at rest.

The above example concerns a special case in that in both fig. 17 and fig. 18 one of the two systems (charged particle or magnet) was assumed to be at rest relative to the ether. We have now to inquire what difference is introduced when both systems have an additional common velocity relative to the ether, as when the whole experiment is carried out in a moving railway carriage. Let us suppose, for instance, that the whole of fig. 17 or 18 is moving through the ether towards the right. Then in consequence of this motion the magnet becomes surrounded by an additional rotational electric field in the sense opposite to that shown in fig. 17, while the charged particle becomes surrounded by an additional rotational magnetic field in the same sense as that shown in fig. 18. The full discussion shows that these two effects exactly cancel out, so that we are left with the same interaction as before. This is only true, however, provided we confine our attention to quantities of the first order. It was shown by Lorentz (compare p. 439) that second-order effects are to be anticipated, on account of the finite velocity of propagation of the alterations of the electromagnetic forces.

Thus the relativity principle is valid for electromagnetic processes, so far as effects of the first order are concerned.

We have already seen (p. 431) that this includes optical processes.

But the negative results of the Michelson-Morley and Trouton-Noble experiments indicate that the motion of the earth produces no effect, even of the second order. It was this which led Einstein to his generalized postulate that the relativity principle is valid for *all* physical processes.

Hypothetical Character of the Relativity Principle.—This generalization of the relativity principle by EINSTEIN is purely hypothetical in character. It involves the assumption that the MICHELSON experiment would give a negative result if performed with an apparatus in uniform rectilinear motion, e.g. in a laboratory moving relative to the earth's surface. An experiment of this kind has never been performed and the result is at present quite an open question. There is not even any indirect evidence for a negative result such as is required by the relativity theory. Nor has any other experiment so far been devised which can allow of a decision between the two alternative views, (*a*) that the ether is carried along by the earth and (*b*) that the relativity principle is of general validity.

4. The Lorentz Transformation, and Einstein's Theory of Relativity

A short account may be given here of the interpretation which Einstein gave of the result of the Michelson-Morley experiment, and which forms the foundation of his "special theory" of relativity.

We know that if a frame of reference in which the space and time co-ordinates of an event are x', y', z', t' is moving with constant velocity v in the direction of the axis of x relative to another frame in which the co-ordinates of the same event are x, y, z, t, then the equations connecting the two sets of co-ordinates may be taken, in Newtonian mechanics, to be

$$x' = x - vt,\ y' = y,\ z' = z,\ t' = t.$$

Now suppose that a wave of light, at the moment when the two origins coincide (i.e. when all the co-ordinates are zero), starts from the common origin. Then the co-ordinates of a point (x, y, z) in the wave front at time t satisfy the equation

$$x^2 + y^2 + z^2 = c^2t^2,$$

for this is the equation of a sphere of radius ct with centre at O the origin. In terms of x', y', z', t', this equation becomes

$$(x' + vt)^2 + y'^2 + z'^2 = c^2t'^2.$$

This is *not* the equation of a sphere with centre at $x' = 0$, $y' = 0$, $z' = 0$. Einstein says that it ought to be so, i.e. that we ought to have

$$x'^2 + y'^2 + z'^2 = c^2t'^2,$$

since the Michelson-Morley experiment shows that the velocity of light is the same in all directions, to the second observer as well as to the first.

There is a set of equations, however, which will secure this result, when they are taken as the equations transforming from the one set of axes to the other. These equations had been used a great deal by Lorentz and Larmor in their researches in electromagnetism, and hence are known as the Larmor-Lorentz transformation, or simply the *Lorentz transformation.* The equations are

$$x' = \frac{x - vt}{\sqrt{(1 - v^2/c^2)}}, \; y' = y, \; z' = z,$$

$$t' = \frac{t - vx/c^2}{\sqrt{(1 - v^2/c^2)}}.$$

It can be verified in a moment that they do actually give

$$x'^2 + y'^2 + z'^2 - c^2t'^2 = x^2 + y^2 + z^2 - c^2t^2.$$

An important point is that the equations still remain true if the accented and non-accented letters are interchanged, provided at the same time v is replaced by $(-v)$. Further, if (X, Y, Z, T) and (X′, Y′, Z′, T′) are the co-ordinates of a second event in the respective systems, and if we write δx for $X - x$, δt for $T - t$, and so on, we get at once by writing down the equations for the second event, and subtracting the original equations from them,

$$\delta x' = \frac{\delta x - v\,\delta t}{\sqrt{(1 - v^2/c^2)}}, \; \delta y' = \delta y, \; \delta z' = \delta z,$$

$$\delta t' = \frac{\delta t - v\,\delta x/c^2}{\sqrt{(1 - v^2/c^2)}}.$$

Hence, in the same way as with the co-ordinates themselves, we have

$$\delta x'^2 + \delta y'^2 + \delta z'^2 - c^2\,\delta t'^2 = \delta x^2 + \delta y^2 + \delta z^2 - c^2\,\delta t^2.$$

In ordinary Newtonian mechanics, in which $\delta t' = \delta t$, this becomes

$$\delta x'^2 + \delta y'^2 + \delta z'^2 = \delta x^2 + \delta y^2 + \delta z^2,$$

which simply states that the *distance* between the two events has the same value in the two systems. The similarity between these two last equations led Minkowski to regard $\sqrt{(\delta x^2 + \delta y^2 + \delta z^2 - c^2\,\delta t^2)}$ as a sort of distance, usually called the *interval,* between the two events in the four-dimensional continuum made up of space and time, and generally called *space-time.* The interval between two events, like the distance between two points in ordinary geometry, has therefore an absolute significance, since the expression for it has the same form in all co-ordinate frames in uniform motion relative to each other.

The outstanding feature of Einstein's interpretation of the Lorentz transformation is that it denies the existence of one absolute time, the same for all observers. Two observers in relative motion make different estimates, not only of the place, but also of the time, at which an event occurs.

The explanation of the Lorentz-Fitzgerald contraction (p. 447), on Einstein's theory, is this. Let the observer A, whose co-ordinates are x, y, z, t, observe two points at the same moment by his clock (so that $\delta t = 0$), and let him estimate the distance between them as δx. The equation

$$\delta x' = \frac{\delta x - v\,\delta t}{\sqrt{(1 - v^2/c^2)}}$$

then gives

$$\delta x' = \frac{\delta x}{\sqrt{(1 - v^2/c^2)}},$$

or

$$\delta x = \sqrt{(1 - v^2/c^2)}\,\delta x'.$$

Now $\delta x'$ is the distance, or length, as estimated by the second observer B. Hence A's estimate of the length is shorter than B's in the ratio $\sqrt{(1 - v^2/c^2)} : 1$. This is the Lorentz contraction.

Similarly, let A estimate the interval of time between two events to be δt, and let these events in his view be at the same place, so that $\delta x = 0$. Then the equation for $\delta t'$ gives

$$\delta t' = \frac{\delta t}{\sqrt{1 - v^2/c^2}}.$$

Thus B considers the interval of time to be longer than A's estimate in the ratio $1 : \sqrt{(1 - v^2/c^2)}$.

Another striking feature of Einstein's theory is its treatment of relative velocity. In ordinary kinematics, if A estimates the velocity of a moving point along the axis of x as V, then B will estimate it as $\mathrm{V} - v$; that is to say, we have

$$\frac{\delta x'}{\delta t'} = \frac{\delta x}{\delta t} - v.$$

In Einstein's theory, however, we have, by the equations for $\delta x'$ and $\delta t'$ written down above

$$\frac{\delta x'}{\delta t'} = \frac{\dfrac{\delta x}{\delta t} - v}{1 - v\dfrac{\delta x}{\delta t}\Big/c^2},$$

which is not the same as before, unless c is infinitely great.

According to Einstein, this equation explains the real origin of Fresnel's "coefficient of drag" (p. 427). Thus, if the velocity of light in a body to which the observer A is attached is $c' = c/n$, where n is the index of refraction of the body, and if the co-ordinates refer to the front of a light wave, then $\delta x/\delta t = c/n$. Hence

$$\begin{aligned}\frac{\delta x'}{\delta t'} &= \frac{c/n - v}{1 - v/nc} \\ &= (c/n - v)(1 + v/nc)\end{aligned}$$

approximately, if v/c is small; that is,

$$\frac{\delta x'}{\delta t'} = \frac{c}{n} - v + \frac{v}{n^2},$$

omitting the term in v^2; or

$$\frac{\delta x'}{\delta t'} = \frac{c}{n} - v\left(1 - \frac{1}{n^2}\right).$$

Since the body is moving with velocity $(-v)$ relative to B, this is precisely Fresnel's result for the velocity of light in the body, as estimated by B.

The "special" theory of relativity refers to empty space, the effects of gravitation or other disturbing influences being neglected. Einstein afterwards developed a "general" theory, in which these influences are taken into account. As in the simple limiting case with which we have been dealing, there is still supposed to be an absolute "interval" between two events. The expression for the interval, however, has a much more general form than $\sqrt{(\delta x^2 + \delta y^2 + \delta z^2 - c^2 \delta t^2)}$, though it is still a quadratic function of the differentials of the co-ordinates. The nature of this function, as also the paths, in space-time, of material bodies, and of light, are determined by conditions specified by Einstein. These conditions are of *invariant* form; that is to say, all observers, no matter what co-ordinates in space-time they may happen to have selected, will derive the same physical results from the conditions specified.

The law of gravitation so derived is, in simple cases, very nearly the same as Newton's law. In fact, Einstein was able to explain by his theory some phenomena which could not be explained by the ordinary Newtonian dynamics.

There is still a good deal of discussion about the exact status of the theory, but the great majority of physicists seem to be agreed in accepting both the special and the general theory in principle, and in using them as the basis of much of their theoretical work.

CHAPTER IX

Matter and Energy in the Universe

1. The Stars and the Universe

The Stellar State of Matter.—Next to the earth, the most important heavenly body for us is the sun (fig. 1). This sphere of matter, which has a mass of $1{\cdot}94 \times 10^{33}$ gm. and a surface temperature of about 6000° C., hangs in space at a mean distance of 149,500,000 kilometres from us. All life on the earth depends for its continuance on the stream of energy sent out by the sun. The total rate of radiation from the sun amounts to $9{\cdot}1 \times 10^{25}$ cal. per second or $3{\cdot}8 \times 10^{33}$ ergs per second. According to the relationship $E = mc^2$, this is equivalent to a mass of $4{\cdot}22 \times 10^{12}$ gm. per second or 133×10^{12} tons per year. We now know from the most varied geological evidence that this rate of radiation has been constant for hundreds of millions of years. In a body like the sun, therefore, we encounter matter in a steady state quite different from that of the ordinary bodies which we investigate in terrestrial laboratories.

The question of the source of this enormous stream of energy has always been a subject of human speculation, but more especially since the recognition of the principle of the conservation of energy. The kinetic energy of cosmic material bodies falling into the sun is quite insufficient; for the terminal velocity of a body falling freely towards the sun is only about 600 kilometres per second at the sun's surface, so that meteorites with a total mass of about one-hundredth of that of the earth would have to fall into the sun every year in order to account for the observed emission of energy. According to Kepler's laws (Vol. I, p. 171), however, this would have resulted in a shortening of our year by about 42 days during the last 2000 years, which is not in agreement with observation. Nor can the emission of energy be explained as due to a condensation of the sun's material, i.e. a transformation of its potential energy in consequence of a shrinkage of its volume. HELMHOLTZ calculated that this explanation would mean that the whole history of the sun's development up to its present state must have taken only 50 million years. In the light of our present knowledge this is certainly much too short a time for the evolution of the solar system. The energy of chemical processes of the kind known on earth is likewise insufficient. If the sun were composed entirely of pure carbon and oxygen, its combustion would only suffice to maintain the observed rate of emission for a few thousands of years.

It is probable, therefore, that the much more energetic nuclear atomic processes (p. 231), similar to the many cases of atomic transmutation which are now known, may be involved; though it appears that even this source of energy, which amounts to about one-thousandth of the masses involved, is insufficient.

This leads to the assumption that processes occur in which material mass is still more completely converted into radiation. According to the relation $E = mc^2$, the rate of radiation from the sun is equivalent to a mass of $1{\cdot}33 \times 10^{20}$ gm. per year, so that (if we assume a constant rate of radiation) its total mass would last for $1{\cdot}5 \times 10^{13}$ years. The age of the sun is estimated to be about 10^{10} years, so that so far it has radiated away only about one-thousandth of its original mass. Such complete transformations of mass into radiation are not known in our laboratories so far, and we must therefore wait for further knowledge. It is by no means inconceivable, for instance, that the energy radiated from stars is derived from some external supply hitherto unknown to us, rather than from the annihilation of the actual stellar material.

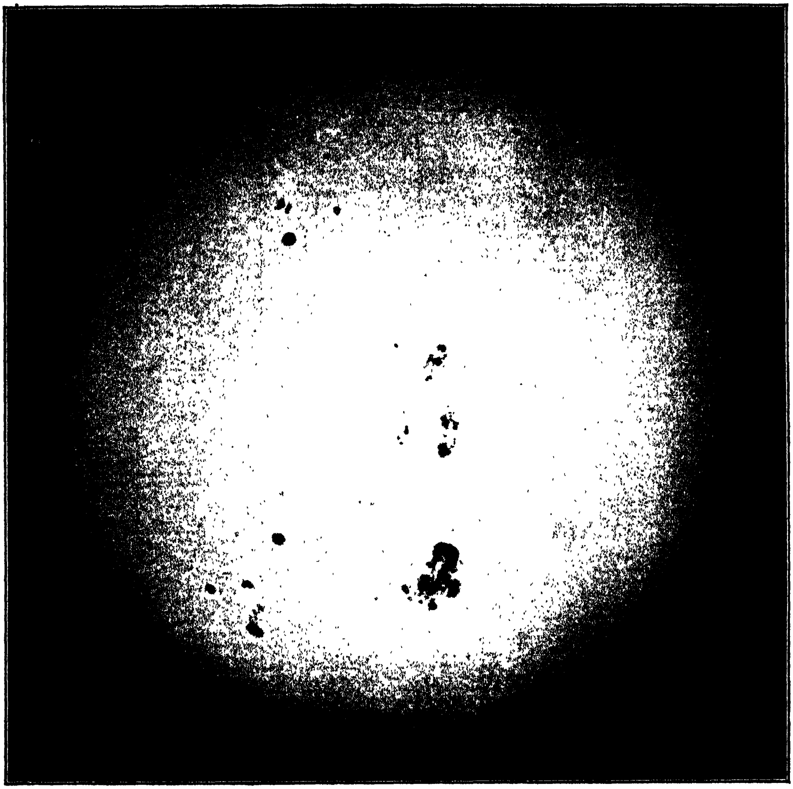

Fig. 1.—The sun, showing sun-spots and faculæ (bright areas). From a photograph taken at Mount Wilson Observatory

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

The Fixed Stars.—As was suspected by Giordano Bruno,* our sun is only one of an enormous number of similar heavenly bodies, the stars. Some of the most important modern evidence for this is derived from the spectra of the stars (fig. 2), many of which are very accurately known. By methods which cannot be discussed here it has been found possible to determine the distances, surface temperatures, sizes, and masses of many stars. One very important result that emerges is that *the masses of the stars which we can observe by the light they emit are of the order of magnitude of* 10^{33} *to* 10^{34} *gm.* This is only a rough mean value, but departures from it by a factor of more than 100 are very rare. Why is it, then, that a mass of this particular magnitude corresponds to a stable, luminous system?

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* Giordano Bruno (*circa* 1548–1600), an Italian philosopher. Forced to leave Italy on account of his religious views, he travelled throughout Europe, visiting England

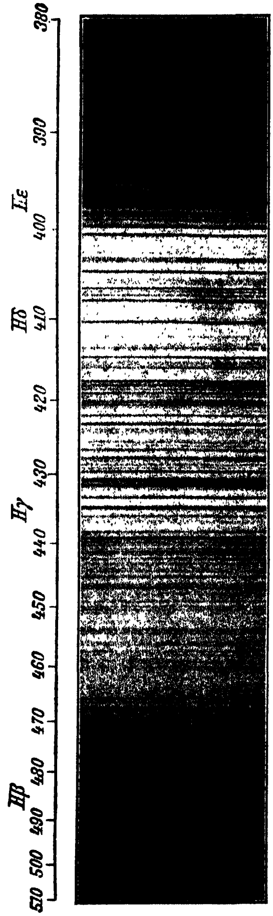

Fig. 2.—Portion of the spectrum of α-Aurigæ (Capella)

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

The most probable picture of a star according to our present-day knowledge is as follows. Matter condenses into a ball, and this gives rise to a high temperature. Even the transformation of potential energy would lead to this result; though, as we pointed out above, this liberation of energy is by no means sufficient to account for the observed facts, and it is necessary to assume much more energetic intra-atomic processes taking place at the high temperatures and pressures of the interior of the shrinking ball of gas. The system so formed, which may have an internal temperature of several million degrees, cannot hold together indefinitely, because the rising temperature brings into action forces which tend to drive the matter outwards and cause it to disperse. These are the forces of *radiation pressure.*

Using data either following from or consistent with modern observations, EDDINGTON * has calculated the way in which the temperature

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1583–5. On his return to his native land he was captured by the Inquisition, and after seven years' imprisonment was burnt at the stake.

* Sir ARTHUR EDDINGTON, born 1882; Professor of Astronomy and Director of the Observatory at Cambridge; knighted in 1930.

and pressure in the interior of such a shrinking ball of gas must depend on the total mass. He arrives at the striking result that for a mass of the order of magnitude of 10^{34} gm. the internal temperature will be such that the radiation pressure will just balance the material pressure (i.e. gravitation minus gas pressure). Stars of larger mass than this would be " blown up " as a result of radiation pressure. (The radiation pressure, being proportional to the energy-density, increases with the fourth power of the temperature (p. 145)). This result applies, independently of density and composition, for a molecular weight of approximately 4, such as may be assumed from the present evidence.

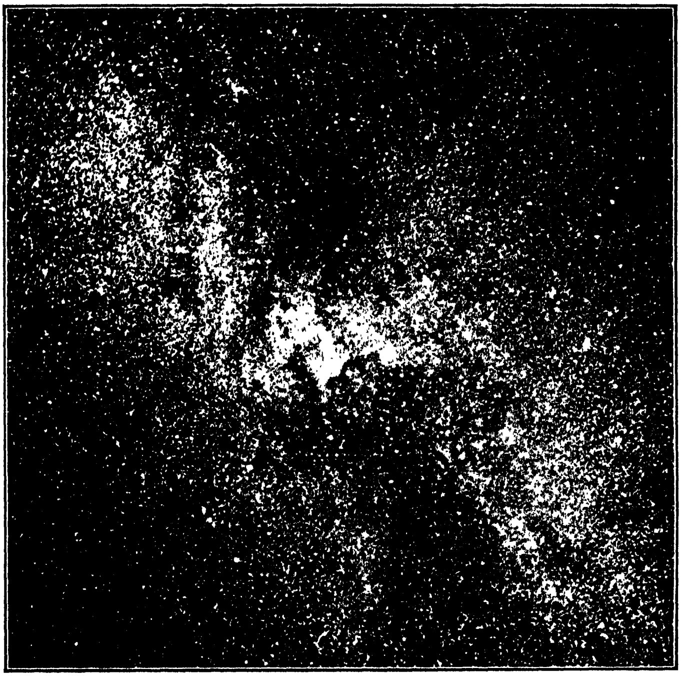

Fig. 3.—The Milky Way in Cepheus and Cygnus (after M. Wolf)

From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

Thus we can understand the existence of the stars, regarding them as assemblages of matter whose form, as far as we can say at present, is maintained by the equilibrium of radiation pressure and gravitational forces, in somewhat the same way as the shape of a drop of mercury lying on the laboratory table is maintained by the equilibrium of surface tension and gravitational forces. In any case, in view of the enormous number of the stars (fig. 3) and the relatively small size and probably also relatively small number of the planets resembling the earth, the modification of matter with which we are ordinarily concerned in terrestrial experiments is probably to be regarded as an exception of extremely rare occurrence in the universe.

Other Modifications of Matter.—Matter can exist in the universe in yet other forms. Enormous regions of space are filled with gases, some of which are excited to luminosity by electrical influences (fig. 4).

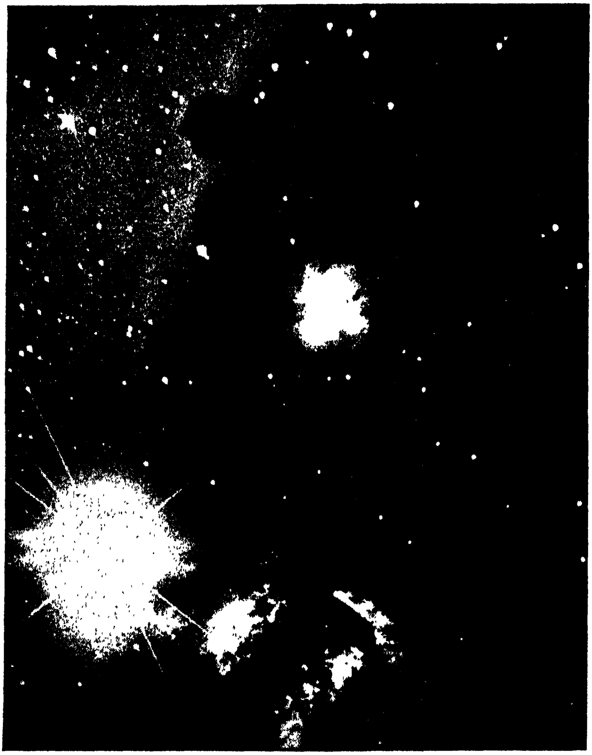

Fig. 4.—Luminous and dark nebulæ to the south of ξ-Orionis (after M. Wolf)

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

Clouds of dust, some illuminated by neighbouring stars, others dark, are also found in the universe. In addition, it is probable that the whole of space, at least in the neighbourhood of our galactic system, is filled with very rarefied gas (about 1 atom per cubic centimetre: possibly Ca and Na).

Higher Cosmic Systems.—In recent times various methods have been worked out whereby the distances of stars situated extremely far away can be determined. These methods furnish some idea of the distribution of stars in space. It is found that the stars are grouped in assemblages, so-called globular star clusters (fig. 5) or spiral nebulæ (figs. 6 and 7). Thus our sun, together with the stars which we see as the Milky Way, belong to a larger system comprising about 3 × 10^9 suns. This system, which may have a form resembling that of a spiral nebula, has a maximum extent of about 30,000 light-years.* The globular clusters appear to be assemblages containing some 10^6 suns within a volume of some hundred light-years diameter. These clusters appear in their turn to form a system co-ordinated with the Milky Way and situated at a distance of about 20,000 light-years from it. The spiral nebulæ are separated by spaces which are large in comparison with the extent of the systems. One of the nearest of them is the nebula in Andromeda, which is just visible to the unaided eye. Its distance from us is about a million light-years, and its diameter in the direction of its major axis is about 50,000 light-years, i.e. about the same as that of the Milky Way system (galactic system) to which we and our sun belong.

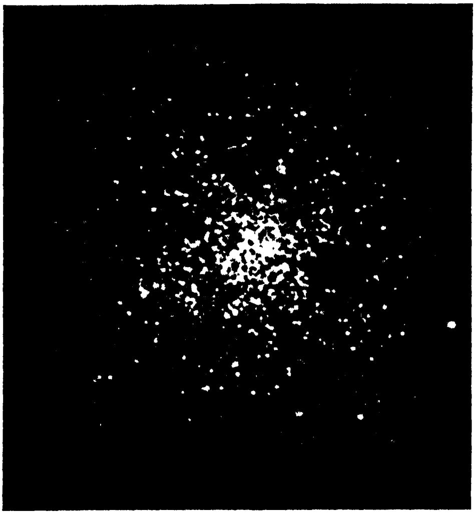

Fig. 5.—Globular cluster M 12 in Ophiuchus
[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

Up to the present, systems of these kinds have been observed with some certainty up to distances of several hundred million light-years. Our knowledge, however, is as yet insufficient to enable us to understand why matter should arrange itself to form globular star clusters or nebulæ.

---

* It is customary to measure astronomical distances in light-years. One light-year is the distance travelled by light in one year, i.e. 9·5 × 10^{16} cm. or 6 × 10^{12} (six million million) miles.

Super-galactic Systems.—It appears that spiral nebulæ are in turn grouped into systems separated by distances which are great in comparison with the size of the individual systems. Among others, mention may be made of such a grouping of about 100 nebulæ in the neighbourhood of the Pole Star. These nebulæ, which are at enormous distances from us (of the order of 10^8 light-years), are all confined to an area of the heavens equal to one-twelfth of that of the full moon.

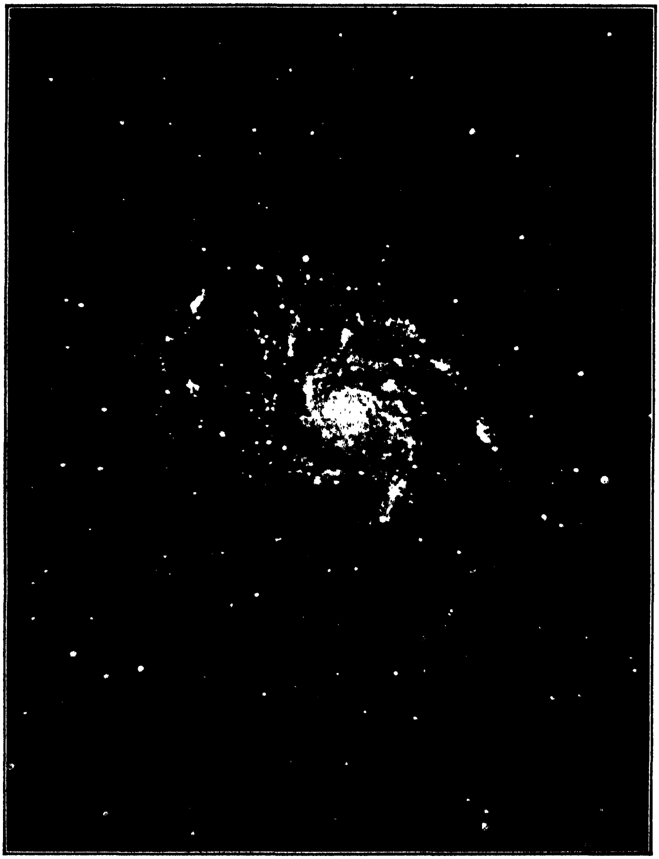

Fig. 6.—Spiral nebula M 101 in Ursa Major (after M. Wolf)

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

One of the most remarkable observations is that the lines in the spectra of these nebulæ exhibit very marked and regular displacements towards the red. The displacements are such that the frequencies of all the lines are diminished in the same ratio. Also, the greater the distance of a nebula from us, the greater is the diminution of frequency (fig. 8). We are still ignorant of the cause of this phenomenon—whether at these tremendous distances the velocity of light has different values or whether the light is modified in the course of its journey lasting hundreds of millions of years. The displacements can be interpreted as a Doppler effect, in which case we are led to the conclusion that the nebulæ must be receding rapidly from us (a so-called expansion of the universe—cf. fig. 8). In the present state of our knowledge, however, it is quite impossible to estimate the probability of this interpretation being the correct one.

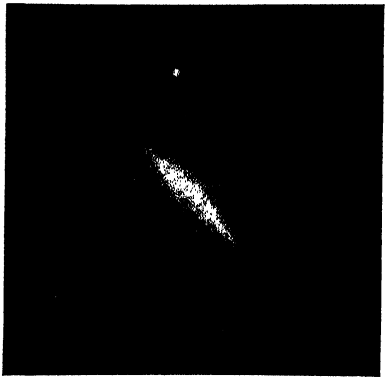

Fig. 7.—Spiral nebula (galactic system) as seen from the side. Photograph of the system NGC 3115 in Sextans, taken at the Mount Wilson Observatory

[From Graff, *Grundriss der Astrophysik* (B. G. Teubner, Leipzig).]

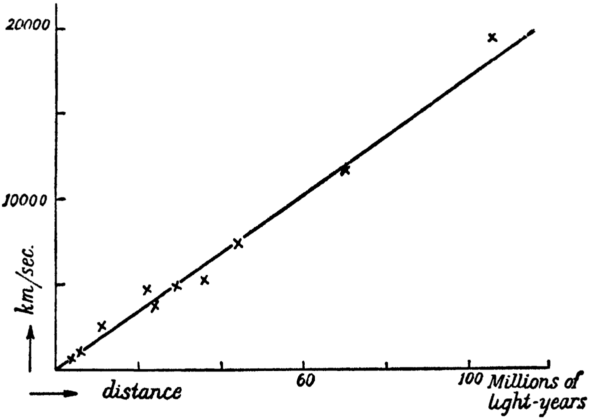

Fig. 8.—Relation between the frequency shift of the light from spiral nebulæ and their distance. The frequency shifts are plotted as velocities, i.e. those velocities which would give rise to an equivalent Doppler effect.

APPENDIX

TABLE OF PHYSICAL CONSTANTS

Velocity of light	$c = (2{\cdot}99796 \pm 0{\cdot}00004) \times 10^{10}$ cm. sec.$^{-1}$.
Fundamental electric constant	$K_0 = 0{\cdot}886 \times 10^{-13} \dfrac{\text{coulomb/cm.}^2}{\text{volt/cm.}}$.
Fundamental magnetic constant	$\mu_0 = 1{\cdot}257 \times 10^{-8} \dfrac{\text{volt sec./cm.}^2}{\text{amp.-turns/cm.}}$.
Electronic charge	$e = (1{\cdot}5911 \pm 0{\cdot}0016) \times 10^{-19}$ abs. coulomb. $= (4{\cdot}770 \pm 0{\cdot}005) \times 10^{-10}$ abs. electrostatic units.
Electronic mass	$m_0 = (9{\cdot}035 \pm 0{\cdot}01) \times 10^{-28}$ gm.
Specific electronic charge	$e/m_0 = (1{\cdot}761 \pm 0{\cdot}001) \times 10^{8}$ coulomb gm.$^{-1}$. $= (5{\cdot}279 \pm 0{\cdot}003) \times 10^{17}$ abs. electrostatic units gm.$^{-1}$.
Planck's constant	$h = (6{\cdot}547 \pm 0{\cdot}008) \times 10^{-27}$ erg sec. $h/(2\pi) = (1{\cdot}0420 \pm 0{\cdot}0013) \times 10^{-27}$ erg sec.
Mass of the proton	$m_P = (1{\cdot}6609 \pm 0{\cdot}0017) \times 10^{-24}$ gm.
Ratio of mass of electron to mass of proton	$m_0/m_P = 1/1839$.
Mass of the hydrogen atom	$m_H = (1{\cdot}6618 \pm 0{\cdot}0017) \times 10^{-24}$ gm.
Mass of the α-particle	$m_\alpha = (6{\cdot}598 \pm 0{\cdot}007) \times 10^{-24}$ gm.
Avogadro's number	$N = (0{\cdot}6064 \pm 0{\cdot}0006) \times 10^{24}$ mol^{-1}.
Gas constant	$R_0 = (8{\cdot}3136 \pm 0{\cdot}001) \times 10^{7}$ ergs degree^{-1} mol^{-1}.
Boltzmann's constant	$k = (1{\cdot}3709 \pm 0{\cdot}0014) \times 10^{-16}$ erg degree^{-1}.
Rydberg constant	$R_H = 109677{\cdot}759 \pm 0{\cdot}05$ cm.$^{-1}$. $R_\infty = 109722{\cdot}403 \pm 0{\cdot}05$ cm.$^{-1}$. $R_\infty c = (3{\cdot}28988 \pm 0{\cdot}00004) \times 10^{15}$ sec.$^{-1}$.
Radiation constant	$c_2 = 1{\cdot}432 \pm 0{\cdot}003$ cm. degree.
Stefan's constant	$\sigma = (5{\cdot}735 \pm 0{\cdot}011) \times 10^{-5}$ erg cm.$^{-2}$ degree^{-4} sec.$^{-1}$.
Fine-structure constant	$\dfrac{2\pi e^2}{hc} = \alpha = (7{\cdot}284 \pm 0{\cdot}006) \times 10^{-3}$. $1/\alpha = 137{\cdot}29 \pm 0{\cdot}11$.
Doublet constant	$R_\infty \alpha^2 = 5{\cdot}822 \pm 0{\cdot}009$ cm.$^{-1}$.
Bohr magneton	$\mu_B = (0{\cdot}920 \pm 0{\cdot}002) \times 10^{-20}$ erg gauss^{-1}.
Zeeman splitting	$\dfrac{\Delta\nu}{H} = \dfrac{e/m}{4\pi c} = (4{\cdot}674 \pm 0{\cdot}003) \times 10^{-5}$ cm.$^{-1}$ gauss^{-1}.
Radius of first circular orbit of the hydrogen atom	$a_0 = (0{\cdot}5285 \pm 0{\cdot}004) \,.\, 10^{-8}$ cm.

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